tions for C(graphite) and H_2(g) given by Wagman *et al.*,[12] and thermodynamic functions for S_2(g) and the value $\Delta H^\circ_{298.16} = 30.84$ kcal. for 2 S(rhombic) = S_2(g), given by Evans and Wagman[13] were used. The calculated values of ΔH°_f, ΔF°_f, and $\log_{10}K_f$ for thiophene are listed in the last three columns of Table III.

Acknowledgment.—The authors wish to thank S. Sunner and B. Lundin[6] for making available an unpublished value of the heat of formation of thiophene.

[12] D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **34**, 143 (1945).

[13] W. H. Evans and D. D. Wagman, *ibid.*, **59**, 141 (1952).

CONTRIBUTION NO. 50 FROM
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The Preparation and Reactions of Dihalotetraalkylditin Compounds[1]

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RECEIVED JUNE 20, 1955

Johnson and Fritz recently reported the preparation of a dihalotetraalkylditin.[2] They obtained dichlorotetra-*n*-butylditin through a coupling of dichlorodi-*n*-butyltin using sodium ethoxide in ethanol.

Further studies of this reaction have revealed that certain organic bases can replace the sodium ethoxide in this coupling. Several amines were used to prepare 1,2-dichlorotetra-*n*-butylditin by mixing equimolar quantities of dichlorodi-*n*-butyltin and the organic base, followed by the addition of a small quantity of alcohol. Immediately following the addition of the ethanol, the crystalline amine hydrochloride separated. Table I lists the amines tested and the yields of the ditin compounds obtained. The evidence suggests that a strong base is necessary to make the reaction proceed.

Several other dihalotetraalkylditin compounds have been synthesized using various amines as condensing agents. Besides 1,2-dichlorotetra-*n*-butylditin which has been previously reported, 1,2-dichlorotetraethylditin, 1,2-dichlorotetra-*n*-propylditin, 1,2-dichlorotetra-*n*-amylditin, 1,2-dichlorotetraphenylditin and 1,2-dibromotetra-*n*-butylditin have been prepared.

The greater reactivity of bromine over chlorine in this coupling reaction was demonstrated by coupling bromochlorodibutyltin. A 92% yield of 1,2-dichlorotetra-*n*-butylditin was isolated. The bromine was cleaved and was isolated in high yield as the amine hydrobromide.

Experimental

Synthesis of Dichlorotetrabutylditin, Using Various Organic Bases.—In general, 0.025 mole of dichlorodibutyltin was mixed with 0.025 mole of the selected base in 50 ml. of anhydrous ether, and 20 ml. of anhydrous ethanol added immediately with stirring. When triethylamine was used, the solution turned slightly yellow on mixing dichlorodibutyltin and the base, and a white precipitate formed which dissolved on stirring. On adding the ethanol a permanent white precipitate of triethylamine hydrochloride (m.p. 254°) was formed in about 98% yield. Evaporation of the slightly yellow filtrate and recrystallization from acetone gave white crystals of dichlorotetrabutylditin, m.p. 110–112°.

Preparation of Individual Ditin Compounds. Preparation of the Et_2SnCl_2 Used as Starting Material.—Tetraethyltin (24.5 g., 0.1026 mole) was mixed with tin tetrachloride (26.6 g., 0.1026 mole) and the mixture warmed to 140°. The solution was then held at 220–230° for three hours and allowed to cool, forming a solid crystalline mass. Recrystallization from 60 ml. of petroleum ether (b.p. 60–68°) gave 8.7 g. of white needle-shaped crystals, m.p. 89°. Leaving the filtrate in a refrigerator for two days produced an additional 18.1 g.; total yield 52%.

Preparation of Dichlorotetraethylditin.—Dichlorodiethyltin (8.7 g., 0.035 mole) was dissolved in 50 ml. of absolute ethanol and a solution of redistilled triethylamine (3.55 g., 0.035 mole) in 25 ml. of absolute ethanol was added within 15 seconds with vigorous stirring. The reaction was slightly exothermic and the temperature of the mixture rose to 35°. After about one minute of stirring a white solid began to separate. The stirring was continued for one hour, then the ethanol was distilled at room temperature under reduced pressure. Anhydrous ether (100 ml.) was added, dissolving part of the white solid. The residual solid was filtered off and the ether removed from the filtrate by distillation leaving 6.3 g. of white residue. The residue was crystallized from acetone, which dissolves any unreacted Et_2SnCl_2. The first crystallization gave 3.0 g. of white crystals. A second crystallization yielded 2.6 g.; total yield 77%.

Anal. Calcd. for $(C_2H_5)_4Sn_2Cl_2$: C, 22.63; H, 4.75; Cl, 16.70. Found: C, 22.45; H, 4.89; Cl, 16.48.

The white crystalline compound turned a slightly tan color when heated in air at 120° for several hours and sublimed at 160°. When a sample was sublimed at 0.1 mm. it decomposed giving $(C_2H_5)_2SnCl_2$ and a white residue melting at about 240°. The $(C_2H_5)_4Sn_2Cl_2$ decomposed and turned brown at about 175° when heated in a capillary melting point tube.

Dichlorotetrapropylditin.—Dichlorodi-*n*-propyltin (13.8 g., 0.05 mole), prepared similarly to dichlorodiethyltin above, was dissolved in 100 ml. of ether, and a solution of hydrazine (1.52 g., 0.05 mole) in 40 ml. of anhydrous ethanol was added. A white precipitate formed immediately. The mixture was stirred for one hour and then filtered yielding 3.2 g. of a white solid which was washed with ether. The ether–ethanol filtrate was evaporated until the odor of ether was no longer discernible, leaving a final volume of about 35 ml. Cooling slowly gave large, soft, odorless white crystals of dichlorotetrapropylditin, m.p. 120.5–121.5°; yield 11.2 g. (93%).

Anal. Calcd. for $(C_3H_7)_4Sn_2Cl_2$: C, 29.96; H, 5.86. Found: C, 29.80; H, 5.33.

The 3.2 g. of white solid obtained by the first filtration was probably a mixture of $N_2H_4 \cdot HCl$, m.p. 89°, $N_2H_4 \cdot 2HCl$, m.p. 198°, and the ditin compound, m.p. 119–122°. It was partially water soluble, sintered at 90–95°, melted to a cloudy white liquid between 150–190° and cleared gradually to a clear liquid at 210–215°.

Dichlorotetraamylditin.—9.93 g. (0.03 mole) of dichlorodi-*n*-amyltin in ether was treated with 0.96 g. (0.03 mole) of hydrazine in alcohol, and the reaction proceeded similarly to the synthesis of dichlorotetrabutylditin. The product was in the form of small white crystals, recrystallized from ethanol, mp. 96.5–97.5°, yield 92.8%.

Anal. Calcd. for $(C_5H_{11})_4Sn_2Cl_2$: C, 40.52; H, 7.48. Found: C, 40.31; H, 7.43.

Dichlorotetraphenylditin.—Dichlorodiphenyltin (10.3 g., 0.03 mole), prepared similarly to dichlorodiethyltin, was dissolved in 60 ml. of ether and a solution of hydrazine (0.96 g., 0.03 mole in 25 ml. anhydrous ethanol) was added. A white precipitate formed immediately. The reaction was slightly exothermic, the temperature of the mixture rising to 35°. Stirring was continued for one hour, the mixture allowed to stand overnight and then filtered yielding 8.2 g. of white powder. The filtrate was evaporated down, and small white crystals were obtained from it.

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[1] This research was supported by the United States Air Force, through the Office of Scientific Research of the Air Research and Development Command.

[2] O. H. Johnson and H. E. Fritz, *J. Org. Chem.*, **19**, 74 (1954).

These were recrystallized from benzene, yielding 1.2 g. of hard, irregular, white crystals, melting with decomposition at 185–187°. More of these crystals were obtained from the precipitate by leaching the solid with water, leaving 6.5 g. of material, and recrystallizing this residue from benzene to give 0.65 g. of product; yield 20%. Considerable decomposition occurred in the process and other solids were also obtained.

Anal. Calcd. for $(C_6H_5)_4Sn_2Cl_2$: C, 46.74; H, 3.27. Found: C, 45.68; H, 3.58.

Dibromotetrabutylditin.—Dibromodi-*n*-butyltin was coupled with triethylamine in ether in the same way as was used for synthesizing the chloro compounds. Triethylamine was precipitated in 98% yield, and from the filtrate a 61% yield of dibromotetrabutylditin was obtained. The compound first appeared as a pale brown solid, but after four recrystallizations from alcohol fine white crystals were obtained which melted at 103–104°.

Anal. Calcd. for $(C_4H_9)_4Sn_2Br_2$: C, 30.65; H, 5.79. Found: C, 30.82; H, 5.84.

Preparation of Bromochlorodibutyltin.—Bromine (4.79 g., 0.03 mole) in 25 ml. of CCl_4 was added dropwise with stirring to 16.12 g. (0.03 mole) of tetrabutyldichloroditin in 75 ml. of CCl_4 and the solution heated on the steam-bath giving a colorless solution after about 30 minutes. The CCl_4 was distilled off leaving 30 ml. of clear slightly yellow liquid. Distillation at 1 mm. yielded a product boiling at 98–104° which crystallized as white needles, m.p. 32.5–35.5°; yield 60%.

Dichlorotetrabutylditin from Bromochlorodibutyltin.—Bromochlorodibutyltin (8.71 g., 0.025 mole) was partially dissolved in 50 ml. of ether and 2.53 g. (0.025 mole) of triethylamine added. A small amount of curdy white precipitate formed immediately. The addition of 10 ml. of anhydrous ethanol caused sufficient heating to make the ether boil and a very thick white solid formed immediately. After stirring for one hour the mixture was filtered and the residue washed with ether. The residue, 4.12 g., was soluble in water and melted, with darkening, at 235–237°, and was apparently impure triethylamine hydrobromide (m.p. 248°).

Evaporating the filtrate and recrystallizing the resulting solid from acetone gave 6.21 g. (92.4%) of dichlorotetrabutylditin.

Analysis for carbon in organotin compounds gives low results on account of the retention of CO_2 by the SnO_2 residue. Colaitis and Lesbre[3] report that this error may be minimized by using silver vanadate during combustion, and this was done in the analyses reported here.

The experimental evidence suggests that a strong organic base is necessary to make the reaction proceed and it was hoped that a relationship would be found between the strength of the base used and the yield of ditin compound obtained. However, no such relationship was immediately apparent, although the weak bases *o*-nitroaniline and pyridine gave a zero yield of product. A summary of yields with various bases is given in Table I.

TABLE I

EFFECT OF BASE ON YIELD OF DICHLOROTETRABUTYLDITIN

Base	Yield of ditin compd., %
Diethanolamine, $(HOC_2H_4)_2NH$	96.1
Hydrazine, N_2H_4	94.5
Triethylamine, $(C_2H_5)_3N$	93.0
p-Aminodimethylaniline, $H_2NC_5H_4N(CH_3)_2$	82.7
Triethanolamine, $(HOC_2H_4)_3N$	82.4
p-Phenetidine,[a] $C_2H_5OC_6H_4NH_2$	76.3
p-Phenetidine, $C_2H_5OC_6H_4NH_2$	74.4
N,N-Diethylaniline, $C_6H_5N(C_2H_5)_2$	70.5
N-Methyl-N-ethylaniline, $C_6H_5N(CH_3)(C_2H_5)$	65.4
N,N-Diethyl-*o*-toluidine, $CH_3C_6H_4N(C_2H_5)_2$	56.6
N,N-Diethyl-*p*-toluidine, $CH_3C_6H_5N(C_2H_5)_2$	51.4
γ-Picoline, $CH_3C_6H_4N$	46.1
o-Nitroaniline, $NOC_6H_4NH_2$	0
Pyridine, C_5H_5N	0

[a] This result was obtained without the presence of ethanol.

Properties and Reactions of Dichlorotetraalkylditin Compounds.—Dihalotetraalkylditin compounds are white in color and appear as friable, crystalline solids, with a faintly bitter odor. The ethyl and propyl homologs may be recrystallized from methanol or ethanol while the tetrabutyl compound recrystallizes readily from acetone. The bromo compounds are generally more soluble in organic solvents than the chloro compounds. The ethyl-, propyl- and butyldichloroditin compounds are readily soluble in benzene and ether in contrast to dichlorotetraphenylditin which is only slightly soluble in hot benzene.

An increase in the size of the alkyl group causes a lowering of the melting point. Thus $Et_4Sn_2Cl_2$ melts at 170–176°, $Pr_4Sn_2Cl_2$ at 120.5–121.5°, and $Bu_4Sn_2Cl_2$ at 111–112°. Replacing the chlorine by bromine gives a still lower melting compound, $Bu_4Sn_2Br_2$, melting at 102–103°. No comparisons were made with aryl groups since $(C_6H_5)_4Sn_2Cl_2$, melting with decomposition at 185–187°, was the only compound of this type prepared.

Completely alkylated ditin compounds are rather easily oxidized by air and are readily affected by moisture. In contrast, the replacement of two alkyl groups by chlorine causes pronounced changes in the stability of the molecule. Dichloroditin compounds are not changed by prolonged exposure to air or moisture. Dichlorotetrabutylditin decomposes when distilled at reduced pressure, dichlorodibutyltin being one of the decomposition products.

The analyses and the reactions indicate that the compounds are dihalotetraalkylditins with the formula $R_4Sn_2Cl_2$. In benzene solution cryoscopic determination of the molecular weight did not give the value 536.8 required by this formula for the tetrabutyl compound but gave a series of values ranging from 1040 in 0.0513 molal solution to 365 in 0.0027 molal solution. Similar results were obtained using dioxane as the solvent.

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(3) D. Colaitis and M. Lesbre, *Bull. soc. chim. France*, 1069 (1952).

The Infrared Spectra of Aromatic Compounds. III. The 1045–1185 Cm.$^{-1}$ Vibration in Monosubstituted Benzenes[1]

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RECEIVED JULY 27, 1955

One of the frequencies of monosubstituted benzenes in the region 1045–1185 cm.$^{-1}$ is found to be sensitive to the nature of the substituent element. The literature contains conflicting evidence concerning the nature of the mode giving rise to this band. Cole and Thompson,[2] using a simplified potential function and assuming a substituent of infinite mass, calculated that the band in the region of 1065 cm.$^{-1}$ for monosubstituted benzenes is a C–H out-of-plane bending vibration. On the

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[1] Work was performed in the Ames Laboratory of the Atomic Energy Commission.

(2) A. R. H. Cole and H. W. Thompson, *Trans. Faraday Soc.*, **46**, 103 (1950).