according to the equation $C_6H_5C(R)HOH + C_6H_5OH = C_6H_5C(R)HC_6H_4OH$ (*p*) + H_2O, where R is methyl, ethyl or phenyl.

2. A relatively large yield from benzhydrol further confirms the hypothesis that unsaturation of carbon atoms adjacent to the alcoholic group increases the reactivity of the hydroxyl group.

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[Contribution from the Chemical Laboratory of Hobart College]

METHYLPHENYL-STANNANES

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Introduction

Derivatives of tetramethyl-stannane are for the most part, liquids or solids of low melting point and are, on the whole, rather reactive. Derivatives of tetraphenyl-stannane, however, are solids of high melting point and, as a rule, are less reactive than the corresponding methyl compounds. From the three mixed methylphenyl-stannanes, $CH_3Sn(C_6H_5)_3$, $(CH_3)_2Sn(C_6H_5)_2$ and $(CH_3)_3SnC_6H_5$, we might expect derivatives having chemical and physical properties intermediate between those of the corresponding derivatives of tetramethyl- and tetraphenyl-stannane. It was for the purpose of later preparing and studying some of these compounds that the preparation of the mixed stannanes was undertaken.

One of the general methods of preparing mixed stannanes consists in treating a solution of sodium alkyl or aryl stannide in liquid ammonia with alkyl or aryl halide as represented by the following equation:[1] $R_3SnNa + R'X = R_3SnR' + NaX$. This is often a most satisfactory method because of the ease of preparation and purification of the product and also because of the high yields obtainable. The success of this type of reaction is dependent upon the nature of the radicals attached to the tin and the halogen atoms. For example, in preparing dimethyldiphenylstannane by the reaction $Na_2Sn(C_6H_5)_2 + 2CH_3I = (CH_3)_2Sn(C_6H_5)_2 + 2NaI$, yields of the purified product as high as 85% of that calculated were obtained. On treating disodium-dimethyl stannide with two molecules of iodobenzene, however, practically no stannane was obtained but a compound was formed which on hydrolysis yielded dimethylstannyl oxide, $(CH_3)_2SnO$. Furthermore, methyl triphenyl-stannane could be made in practically quantitative yields by the reaction $NaSn(C_6H_5)_3 + CH_3I = CH_3Sn(C_6H_5)_3 + NaI$, while treating sodium-trimethyl stannide with iodobenzene gave a product containing approximately 14% of the stannane and 86% of the nitride, $[(CH_3)_3Sn]_3N$. The main reaction in this case is $3NaSn(CH_3)_3 + 3C_6H_5I + NH_3 = [(CH_3)_3Sn]_3N + 3C_6H_6 + 3NaI$.

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[1] Kraus and Sessions, This Journal, **47**, 2365 (1925).

Preparation of Materials

Trimethylstannyl bromide was prepared according to the method of Kraus and Sessions.[1] The ammonia solution was made by condensing ammonia directly on the bromide instead of using the ammonia addition product of the bromide.

Dimethylstannyl dibromide was made according to the method of Kraus and Greer.[2]

Triphenylstannyl iodide was prepared by treating one equivalent of tetraphenyl-stannane with two atoms of iodine in carbon tetrachloride solution as described by Chambers and Scherer.[3] After removing the carbon tetrachloride and phenyl iodide by distillation under reduced pressure, the crystals of triphenylstannyl iodide were extracted with ether to separate from unchanged tetraphenyl-stannane. On recrystallization from ether, crystals of the iodide were obtained which melted at 120–121°, as stated by Krause;[4] yield, 60%.

Diphenylstannyl di-iodide, $(C_6H_5)_2SnI_2$, was prepared as follows.

Four atoms of powdered iodine were added to solid tetraphenyl-stannane. The dry mixture was well stirred and allowed to stand. In a few minutes the mixture suddenly became liquid, and considerable heat was evolved. On standing overnight, the brown liquid assumed an amber color, and was then distilled under reduced pressure. After the phenyl iodide had been removed, the pressure was reduced to 2 mm. and the diphenylstannyl di-iodide distilled, undecomposed, at 176–182°. The distillate was crystallized from light petroleum ether. Colorless crystals melting at 71–72° were obtained. From 10 g. of tetraphenyl-stannane 7 g. of the pure product was obtained; yield, 57%. When the compound was allowed to stand in the light it turned yellow. It was soluble in the common organic solvents.

Anal. Subs., 0.2255, 0.2505: SnO_2, 0.0650, 0.0720. Calcd. for $(C_6H_5)_2SnI_2$: Sn, 22.54. Found: 22.70, 22.64.

This substance has been previously made by Aronheim[5] in the impure state only, by treating diphenylstannyl oxide with hydrogen iodide.

The Mixed Methylphenyl-stannanes

Methyltriphenyl-stannane, $CH_3Sn(C_6H_5)_3$.—This compound has previously been prepared by Krause and Schmitz[6] by use of the Grignard reaction. The following method of preparation may also be used to advantage.

Triphenylstannyl iodide was dissolved in liquid ammonia and converted into the sodium salt by adding two atoms of sodium per mole of iodide. On adding methyl iodide slowly, a white precipitate formed. The reaction took place according to the equation $NaSn(C_6H_5)_3 + CH_3I = CH_3Sn(C_6H_5)_3 + NaI$. The ammonia was allowed to evaporate, and water was added to dissolve the sodium iodide. The residual white

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[2] Kraus and Greer, THIS JOURNAL, **47**, 2568 (1925).

[3] Chambers and Scherer, *ibid.*, **48**, 1054 (1926).

[4] Krause, *Ber.*, **51**, 913 (1918).

[5] Aronheim, *Ann.*, **194**, 145 (1878).

[6] Krause and Schmitz, *Ber.*, **52**, 2150 (1919).

powder was dried, dissolved in ether, and filtered from any mechanical impurities. After expelling the ether, the pure stannane remained. From 9.45 g. of triphenylstannyl iodide, 6.5 g. of methyltriphenyl-stannane was obtained; yield, 90%. This material melted at 60–61°, which agrees with the melting point given by Krause and Schmitz.[6] The substance is soluble in the common organic solvents.

Anal. Subs., 0.3197, 0.2009: SnO_2, 0.1324, 0.0831. Calcd. for $CH_3Sn(C_6H_5)_3$: Sn, 32.54. Found: 32.62, 32.58.

Dimethyldiphenyl-stannane, $(CH_3)_2Sn(C_6H_5)_2$.—The preparation of this compound from disodium-dimethyl stannide and bromobenzene in liquid ammonia was first tried. Disodium-dimethyl stannide was prepared from dimethylstannyl dibromide by adding the calculated weight of sodium to the ammonia solution of the dibromide. The calculated quantity of bromobenzene was added and the ammonia was allowed to evaporate. Water was added. A dirty white powder remained which was insoluble in all neutral solvents.

Anal. Subs., 0.2469, 0.1429: SnO_2, 0.2253, 0.1294. Calcd. for $(CH_3)_2SnO$: Sn, 72.07. Found: 71.87, 71.33.

A portion of this white powder was treated with dil. hydrochloric acid and the resulting solution was evaporated to dryness. The solid which remained melted at 108–109°. According to Pfeiffer,[7] dimethylstannyl dichloride melts at 109°. Therefore, the reaction of disodium-dimethyl stannide with bromobenzene does not give the stannane but yields presumably a nitrogen compound which reacts with the water added to form dimethylstannyl oxide.

The converse of the above reaction was then tried. Disodium-diphenyl stannide was formed from diphenylstannyl di-iodide and sodium in liquid ammonia, and methyl iodide was added in excess. After evaporating the ammonia, water was added. The stannane separated as a heavy oil. Light petroleum ether was added and the ether solution of the stannane was separated, dried over calcium chloride and filtered. The petroleum ether was removed by distilling under reduced pressure at room temperature. A clear, colorless, heavy oil remained.

Anal. Subs., 0.4994, 0.4044: SnO_2, 0.2486, 0.2009. Calcd. for $(CH_3)_2Sn(C_6H_5)_2$: Sn, 39.21. Found: 39.21, 39.01.

Mol. wt. Subs., 0.4381, 0.5167; in C_6H_6, 23.62, 23.62: Δt, 0.304, 0.356. Calcd. for $(CH_3)_2Sn(C_6H_5)_2$: mol. wt., 302.8. Found: 305, 307; av., 306.

From 10 g. of diphenylstannyl di-iodide 5.7 g. of the stannane was obtained; yield, 84%. The substance was cooled to determine its melting point. As the temperature was lowered it became more viscous, and at —55° was so viscous that it could no longer be stirred. It distilled with decomposition at 127–140° under a pressure of 3 mm. The fact that the compound cannot be purified by either crystallization or distillation renders the Grignard method of preparation impracticable.

Trimethylphenyl-stannane, $(CH_3)_3SnC_6H_5$.—It was at first expected that this compound could be made by treating sodium trimethyl stannide with bromobenzene in liquid ammonia, since it has been shown by Kraus and Sessions[1] that sodium-trimethyl stannide and *p*-dichlorobenzene react to form *p*-$C_6H_4[Sn(CH_3)_3]_2$. Accordingly, trimethyl stannyl bromide was converted into the sodium salt in ammonia, and slightly less than the calculated quantity of bromobenzene was added. During the addition of the bromobenzene, a vigorous reaction took place and a white precipitate was formed. After the reaction, the ammonia was allowed to evaporate and water was added. Complete solution of the reaction products, with the exception of an oily film, resulted. The second preparation was carried out like the first except that after the evaporation of the

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[7] Pfeiffer, *Z. anorg. Chem.*, **68**, 102 (1910).

ammonia, the residue was extracted with ether, and the extract filtered. It was then allowed to evaporate spontaneously. A white, crystalline powder, melting with slight decomposition at 118–118.8°, was obtained.

Anal. Subs., 0.1630, 0.1742: SnO_2, 0.1366, 0.1457. Calcd. for $(CH_3)_3SnOH$: Sn, 65.69. Found: 66.00, 65.88.

This powder was recrystallized from chloroform. The large crystals thus formed were decomposed by heating in a vacuum in order to determine if these were trimethylstannyl hydroxide. Two liquids formed in the distillate and a solid white residue remained. The original substance sublimed to some extent. One of the liquids was solid at liquid ammonia temperature and reacted with sodium, indicating water. The other liquid boiled at 77–78°, the boiling point of tetramethyl-stannane. The molecular weight of the vapor of this liquid was determined.

Mol. wt. Subs., 0.2152: 332.3 cc. (67.1 mm., 30°). Calcd. for $(CH_3)_4Sn$: mol. wt., 178.8. Found: 182.3.

The residual powder did not melt on heating. Analysis showed it to be dimethylstannyl oxide.

Anal. Subs., 0.0123, 0.0287: SnO_2, 0.0113, 0.0264. Calcd. for $(CH_3)_2SnO$: Sn, 72.07. Found: 72.28, 72.45.

The products formed on heating these crystals are identical with those formed on heating trimethylstannyl hydroxide under the same conditions.[8]

To account for the presence of trimethylstannyl hydroxide in the product, it seemed necessary to assume the formation of some nitrogen compound which hydrolyzed in the air, yielding trimethylstannyl hydroxide. In the next preparations, the substance was extracted in the reaction tube with dry petroleum ether, after the ammonia had been allowed to evaporate. The extract was siphoned off in the absence of air and the petroleum ether was removed by boiling under reduced pressure at room temperature. At the end, the pressure was reduced to about 1 mm. The material thus prepared was sealed in tubes under dry nitrogen. The following analyses were made of material from several preparations.

Anal. (Carius method.) Subs., 0.4743, 0.6012, 0.6058, 0.4552: SnO_2, 0.4107, 0.5115, 0.5159, 0.3928. Found: Sn, 68.20, 67.01, 67.09, 67.97; av., 67.57. (Kjeldahl method.) Found: N, 2.31, 2.32, 2.40, 2.42, 2.44, 2.36, 2.37; av., 2.37.

Since the above analytical results do not agree with any formula, it seemed probable that the nitrogen compound was mixed with some of the stannane. To confirm this, a large amount of the product was made and the tubes containing it were broken beneath water. A vigorous reaction took place and a few drops of a heavy oil were formed. This was removed and its boiling point determined. It boiled at 200–205° under atmospheric pressure. The stannane, $(CH_3)_3SnC_6H_5$, prepared by the Grignard reaction, boils at 203–208°. Hence, this preparation consists of a mixture of a nitrogen compound and the stannane. If we assume that the nitrogen compound is represented by the formula $[(CH_3)_3Sn]_3N$, then, calculating from the nitrogen content of the product as

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[8] Bullard, *Dissertation*, Brown University, 1925.

found, we see that the mixture consists of 85.7% of $[(CH_3)_3Sn]_3N$ and 14.3% of $(CH_3)_3SnC_6H_5$. Such a mixture would have a calculated tin content of 67.44%; found, 67.57%. Hence, while the stannane is formed to some extent, the main reaction is apparently represented by the equation, $3(CH_3)_3SnNa + 3C_6H_5Br + NH_3 = [(CH_3)_3Sn]_3N + 3C_6H_6 + 3NaBr$. That benzene is formed in this reaction was shown by the following experiment.

After completing the reaction and evaporating the ammonia, the reaction tube was connected to a receiver immersed in liquid ammonia and the system was evacuated. The reaction tube was warmed in a water-bath to 50° and a solid appeared in the receiver. This distillate had the odor of benzene and distilled completely at 78–80°.

If chlorobenzene is used in place of bromobenzene the reaction is exceedingly slow, but if iodobenzene is used it is very vigorous. The same end products in the same proportions are formed.

The stannane was then prepared by means of the Grignard reaction. The calculated quantity of the trimethylstannyl bromide in dry benzene was slowly added to phenylmagnesium bromide in absolute ether. The mixture was then refluxed for several hours. The ether was distilled and water added to the residue. The lower layer of oil was separated, dried over calcium chloride and distilled. The fraction boiling at 200–210° was collected. On redistillation, the fraction boiling at 203–208° was collected as the pure stannane; yield, 35%. The compound is a clear, colorless oil having a pleasant odor.

Anal. Subs., 0.1874: SnO_2, 0.1167. Calcd. for $(CH_3)_3SnC_6H_5$: Sn, 49.29. Found: 49.05.

Mol. wt. Subs., 1.3723, 0.1231, 0.7620: in C_6H_6, 17.10, 19.34, 21.00: Δt, 1.698, 0.1315, 0.777. Calcd. for $(CH_3)_3SnC_6H_5$: mol. wt., 240.7. Found: 236.3, 242.2, 233.5; av., 237.3.

Bromination of Trimethylphenyl-stannane.—The stannane was brominated by adding to its benzene solution, cooled in ice water, a carbon tetrachloride solution of two atoms of bromine per mole of stannane. Bromination took place instantly. On passing ammonia gas into the solution a white precipitate appeared, which was filtered and dried.

Anal. Subs., 0.1286, 0.1451: SnO_2, 0.0741, 0.0835. Calcd. for $(CH_3)_3SnBrNH_3$: Sn, 45.56. Found: 45.38, 45.33.

The filtrate was then distilled. After removal of the benzene and carbon tetrachloride, the thermometer rose suddenly to 156° and the remaining liquid distilled. Phenyl bromide boils at 156°; hence, the bromination of trimethylphenyl-stannane results in the removal of the phenyl group, the reaction proceeding according to the equation $(CH_3)_3SnC_6H_5 + Br_2 = (CH_3)_3SnBr + C_6H_5Br$. These results agree with Aronheim's statement that the phenyl group is loosely bound to tin.[5]

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Summary

1. Diphenylstannyl di-iodide has been prepared in the pure state in yields of 57%.

2. Methyltriphenyl-stannane has been prepared in practically quanti-

tative yields by treating sodium-triphenyl stannide in liquid ammonia with methyl iodide.

3. Dimethyldiphenyl-stannane has been prepared by treating disodium-diphenyl stannide in liquid ammonia with methyl iodide. Treating disodium-dimethyl stannide with phenyl bromide does not give the stannane.

4. Trimethylphenyl-stannane has been prepared by the Grignard reaction. Treatment of sodium-trimethyl stannide with phenyl bromide gives a product consisting of 86% of trimethylstannyl nitride, $[(CH_3)_3Sn]_3N$, and 14% of trimethylphenyl-stannane, $(CH_3)_3SnC_6H_5$.

5. On brominating trimethylphenyl-stannane, the phenyl group is removed.

GENEVA, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY, NO. 540]

RESEARCHES ON THIAZOLES. XIII. THE SYNTHESIS OF 2-ARYL 6-DIMETHYLAMINO-BENZOTHIAZOLES FROM 2-AMINO-5-DIMETHYLANILINE THIOSULFURIC ACID AND AROMATIC ALDEHYDES[1]

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Introduction

Confusion has crept into the literature through the failure of authors to discriminate between thiosulfuric acids, $RSSO_2OH$, and thiosulfonic acids, RSO_2SH, when naming their products, the former frequently being incorrectly designated as thiosulfonic acids.

In the course of his classical work upon the structure of Methylene Red and Methylene Blue, Bernthsen[2] had occasion to prepare and study the monothiosulfuric acids from *p*-phenylenediamine, *p*-aminodimethyl- and -diethylaniline and tetramethyl-*p*-phenylenediamine, and in a subsequent paper[3] described 2-N-dimethyl and diethyl derivatives of 2,5-diaminotoluene.

He was led to undertake this investigation because of the patents taken out by Roth[4] covering the manufacture of blue dyes from the hydrochlorides of *p*-amino dialkyl anilines and of dialkyl anilines, sodium thiosulfate and potassium dichromate. On the assumption that the intermediate product in this reaction was a thiosulfuric acid of one of the amines, which in turn condensed with a second mole of amine to a thiazine,

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[1] Presented in abstract before the Organic Division of the American Chemical Society at its Richmond Meeting, April, 1927.

[2] Bernthsen, *Ann.*, **251**, 1–97 (1889).

[3] Bernthsen, *Ber.*, **25**, 3128 (1892).

[4] Roth, Ger. pat. 38,573 (1885); *Winther*, **2**, 452 (1908).