the reaction has sufficient advantages over other methods, one of which involves the Grignard reagent.[25]

The reaction may find some application in the preparation of substituted hydrazo compounds, where the corresponding hydrazo compounds are very unstable. The —MgX groups on the two nitrogens are undoubtedly capable of undergoing many of the reactions of Grignard reagents. These salts are more accessible than the alkali metal salts of Schlenk.[26]

Because of the apparently different rates of reaction between RMgX compounds and azobenzene it may be possible to determine the relative reactivities of Grignard reagents, inasmuch as all RMgX reactions involve at some stage a dissociation into R and —MgX.[27]

## Summary

It has been proved that the following reaction takes place between azobenzene and the Grignard reagent. $C_6H_5N{=}NC_6H_5 + 2RMgX \longrightarrow C_6H_5N(MgX)N(MgX)C_6H_5 + R\text{-}R$.

AMES, IOWA

# COMPOUNDS FORMED BETWEEN TRIMETHYLTIN HYDROXIDE AND TRIMETHYLTIN HALIDES

BY CHARLES A. KRAUS AND T. HARADA

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Callis[1] has observed that under the action of sunlight, trimethyltin iodide acquires a brown color which slowly disappears in the dark. After some time, crystals are formed which at times are contaminated by other products. Callis showed that oxygen is absorbed in the course of the reaction. The brown color is apparently due to iodine which is displaced from the compound by oxygen under the action of sunlight.

It was thought worth while to study the crystalline product formed in this photochemical reaction. It was found that the disappearance of color, when the iodide is removed from the action of light, is due to the presence of tetramethyltin as impurity. In the absence of sunlight, the iodine, previously formed, slowly reacts with the tetramethyltin to form trimethyltin iodide and methyl iodide, according to a well-known reaction. The compound formed, which crystallizes in the form of needles, is readily soluble in water and absolute alcohol and only slightly soluble in such organic solvents as benzene and ether. Its aqueous solutions are strongly acidic, indicating a relatively high degree of hydrolysis.

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[25] Gilman and Parker, THIS JOURNAL, **46,** 2823 (1924).

[26] Schlenk, Appenrodt, Michael and Thal, *Ber.*, **47,** 473 (1914).

[27] Kondyrew [*Ber.*, **58,** 459 (1925)] is now studying the conductivities of RMgX compounds.

[1] Callis, *Dissertation,* Clark University, 1922.

It was thought that, initially, iodine is substituted by oxygen according to the equation $2(CH_3)_3SnI + {}^1/_2O_2 = [(CH_3)_3Sn]_2O + I_2$. In view of the known tendency of oxygen to form compounds of the oxonium type, it was thought that an oxonium compound might be formed by combination of trimethyl tin oxide with trimethyltin iodide according to the equation, $[(CH_3)_3Sn]_2O + (CH_3)_3SnI = [(CH_3)_3Sn]_3OI$. When the compound was analyzed for iodine, however, a value in the neighborhood of 19.5% was obtained in place of 20.01 as required for a compound of the oxonium type. Analysis for tin indicated the presence of three atoms of tin per atom of iodine. These analyses were repeated many times with the same result and it was concluded, therefore, that the proposed formula is inapplicable. The presence of water was suspected. It was found that when trimethyltin iodide is treated with two molecular proportions of trimethyltin hydroxide, a crystalline product results whose properties appear to be identical with those of the compound ordinarily obtained by the action of sunlight and which, on analysis, yielded similar results. It appeared, therefore, that the formula of the compound is $[(CH_3)_3SnOH]_2\cdot(CH_3)_3SnI$, which contains 19.46% of iodine. The precise nature of this compound remains uncertain. Further discussion of its properties will be presented in a subsequent paper.

Other trimethyltin halides, when treated with oxygen in sunlight, or with trimethyltin hydroxide in benzene, were found to yield similar compounds. The compounds in question are quite stable until the melting point is reached, when decomposition occurs as fusion sets in. The point of decomposition is fairly sharp, being about 150° for the iodide and 115° for the bromide.

When trimethyltin iodide is treated with one molecular proportion of trimethyltin hydroxide under suitable conditions, a crystalline product is formed which again is readily soluble in alcohol and water and difficultly soluble in the usual organic solvents. The formula for this compound appears to be $(CH_3)_3SnOH\cdot(CH_3)_3SnI\cdot H_2O$. Similar compounds were obtained with the chloride and the bromide.

All three compounds crystallize readily, large, lustrous crystals often being obtained. Their ready solubility in ionizing solvents and their insolubility in non-polar solvents indicates that they are salt-like substances.

## Experimental Part

$[(CH_3)_3SnOH]_2\cdot(CH_3)_3SnI$. **Preparation A.**—Trimethyltin iodide was dissolved in tetramethyltin and exposed to air under the action of sunlight. After some days, needle-like crystals were formed. These were washed with petroleum ether to remove trimethyltin iodide. The crystals were found to be readily soluble in water, alcohol and acetone, and insoluble in benzene and similar solvents. They melt with decomposition at 143–153°, depending upon the rate of heating.

*Anal.* Subs., 0.1079, 0.5794: AgI, 0.0387; $SnO_2$, 0.4502. Calcd. for $C_9H_{29}O_2Sn_3I$: I, 19.46; Sn, 54.59. Found: I, 19.45; Sn, 55.08.

**Preparation B.**—A quantity of the free trimethyltin group, $(CH_3)_3Sn$, was dissolved in moist benzene, along with trimethyltin iodide, and this solution subjected to oxidation in the dark. After some days, crystals appeared, whose properties were similar to those of Preparation A.

*Anal.* Subs., 0.1982, 0.2419: AgI, 0.0712, 0.0872. Calcd. for $C_9H_{29}O_2Sn_3I$: I, 19.46. Found: 19.43, 19.49.

**Preparation C.**—Trimethyltin iodide was treated with two molecular proportions of trimethyltin hydroxide in hot benzene solution. Needle-like crystals were precipitated. The properties of these needles were found to correspond with those of Preparations A and B.

*Anal.* Subs., 0.2199, 0.5169, 0.2379, 0.3617: AgI, 0.0797, 0.1857, 0.0863, 0.1301. Calcd. for $C_9H_{29}O_2Sn_3I$: I, 19.46. Found: 19.59, 19.42, 19.61, 19.44 (av. 19.52).

Subs., 0.3244, 0.3777, 0.3776, 0.4316, 0.2120: $SnO_2$, 0.2245, 0.2640, 0.2621, 0.3008, 0.1493. Calcd. for $C_9H_{29}O_2Sn_3I$: Sn, 54.59. Found (Carius): 54.51, 55.05, 54.67 54.90, 55.57 (av., 54.92).

$[(CH_3)_3SnOH]_2\cdot(CH_3)_3SnBr$. **Preparation A.**—Trimethyltin bromide dissolved in tetramethyltin was exposed to air in sunlight. Needle-like crystals appeared; m. p., 113–115°, with decomposition. The compound is readily soluble in water and alcohol and insoluble in benzene and similar solvents.

*Anal.* Subs., 0.3712, 0.4735: AgBr, 0.1148, 0.1451. Calcd. for $C_9H_{29}O_2Sn_3Br$: Br, 13.20. Found: 13.16, 13.05.

**Preparation B.**—This compound was prepared as was the corresponding iodide, by the oxidation of the free group in the presence of trimethyltin bromide in moist benzene solution. Needle-like crystals were formed; m. p., 113–115°, with decomposition. The compound is readily soluble in water and alcohol and insoluble in non-polar organic solvents.

*Anal.* Subs., 0.6037: AgBr, 0.1874. Calcd. for $C_9H_{29}O_2Sn_3Br$: Br, 13.20. Found: 13.21.

**Preparation C.**—Trimethyltin bromide was treated with two molecular proportions of trimethyltin hydroxide in hot benzene. Crystals were immediately precipitated having properties identical with those of Preparations A and B.

*Anal.* Subs., 0.2996: AgBr, 0.0933. Calcd. for $C_9H_{29}O_2Sn_3Br$: Br, 13.20. Found: 13.25.

$[(CH_3)_3SnOH]_2\cdot(CH_3)_3SnCl$.—Two molecular proportions of trimethyltin hydroxide were treated with one molecular proportion of trimethyltin chloride in hot benzene. Needle-like crystals were formed which were found to be readily soluble in water and alcohol and insoluble in benzene and similar solvents.

*Anal.* Subs., 0.3329: AgCl, 0.0843. Calcd. for $C_9H_{29}O_2Sn_3Cl$: Cl, 6.32. Found: 6.26.

$(CH_3)_3SnOH\cdot(CH_3)_3SnI\cdot H_2O$.—This compound was prepared by treating trimethyltin iodide with trimethyltin hydroxide (1 molecular proportion) in hot alcohol and allowing the resulting solution to stand for some days at room temperature while crystals separated. It was recrystallized from alcohol; m. p., 221° with decomposition. They are markedly less soluble in water and alcohol than are the compounds of the type $(Me_3SnOH)_2\cdot Me_3SnX$. They are insoluble in benzene and similar solvents.

*Anal.* Subs., 0.1199, 0.1320, 0.3050, 0.4074: AgI, 0.0586, 0.0635; $SnO_2$, 0.1922, 0.2559. Calcd. for $C_6H_{19}OSn_2I\cdot H_2O$: I, 25.93; Sn, 48.50. Found: I, 26.42, 26.00; Sn, 49.62, 49.48.

$(CH_3)_3SnOH\cdot(CH_3)_3SnBr\cdot H_2O$.—This compound was prepared as was the corresponding iodide, by treating trimethyltin hydroxide with trimethyltin bromide in hot alcoholic solution; m. p., 210–211° with decomposition. This compound is less soluble in water and alcohol than is the corresponding compound containing two molecules of the hydroxide. It is insoluble in benzene.

*Anal.* Subs., 0.1933, 0.2317, 0.2213: AgBr, 0.0846, 0.0995, 0.0945. Calcd. for $C_6H_{19}OSn_2Br_2{\cdot}H_2O$: Br, 18.06. Found: 18.63, 18.27, 18.17.

$(CH_3)_3SnOH{\cdot}(CH_3)_3SnCl{\cdot}H_2O$.—This compound was prepared as was the corresponding iodide and bromide. The crystals are more difficultly soluble in water than are those of the corresponding compound containing two molecules of hydroxide. They melt at approximately 90°, where decomposition takes place only slowly.

*Anal.* Subs., 0.4550, 0.2065: AgCl, 0.1972, 0.0473. Calcd. for $C_6H_{19}OSn_2Cl{\cdot}H_2O$: Cl, 8.90. Found: 8.95, 8.90.

## Summary

1. Compounds corresponding to the empirical formula $[(CH_3)_3SnOH]_2{\cdot}(CH_3)_3SnX$ have been prepared by the following methods: (1) by subjecting trimethyltin iodide to the action of sunlight in the presence of air; (2) by oxidizing a solution of the free trimethyltin group in moist benzene in the presence of trimethyltin iodide; and (3) by treating trimethyltin halide with 2 molecular proportions of trimethyltin hydroxide in benzene solution. The three preparations yield identical products. The compounds exhibit salt-like properties, being readily soluble in water and alcohol and difficultly soluble in non-ionizing solvents. They melt with decomposition at temperatures above 100°.

2. Compounds of the type $(CH_3)_3SnOH{\cdot}(CH_3)_3SnX{\cdot}H_2O$ have been prepared by treating 1 molecular proportion of trimethyltin hydroxide with 1 molecular proportion of the corresponding halide in alcoholic solution. The compounds are salt-like in properties, are soluble in alcohol and water and insoluble in non-ionizing solvents.

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[Contribution from the Chemical Laboratory of West Virginia University]

# CHLORO ETHERS. II. PREPARATION OF SOME NEW CHLORO ETHERS AND ALKOXYMETHYL ESTERS

By J. W. Farren and H. R. Fife[1] with F. E. Clark and C. E. Garland

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In a previous article[2] from this Laboratory Clark, Cox and Mack have described a series of esters prepared by the action of chlorodimethyl ether on the salts of formic, acetic, propionic and butyric acids. A continuation of this work has led to a study of other chloro ethers of this same series of

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[1] This article is an abstract from theses submitted by J. W. Farren and H. R. Fife for degrees of Master of Science at West Virginia University. A preliminary paper was presented before the Organic Division at the 69th Meeting of the American Chemical Society, April 6–10, 1925 (by F. E. Clark).

[2] Clark, Cox and Mack, This Journal, **39**, 712 (1917).