REACTION OF HYDROTRIPHENYLTIN WITH OXYGEN
AND WITH SOME HALOGEN-CONTAINING
ORGANIC AND INORGANIC COMPOUNDS

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It is known that hydrotriphenyltin is able to convert organic halogen compounds and amines into the corresponding hydrocarbons with formation of halotriphenyltin and hexaphenylditin respectively [1-3]. These reactions occur with the transfer of a hydride ion [4].

We have now studied the reaction of hydrotriphenyltin with oxygen and with some organic and inorganic halogen-containing compounds. We investigated the reaction of hydrotriphenyltin with oxygen in absence and in presence of traces of benzoyl peroxide and traces of hydroquinone. It was shown that with oxygen hydrotriphenyltin reacts in accordance with the scheme

\[ 4(C_6H_5)_3SnH + O_2 \rightarrow 2(C_6H_5)_3Sn - Sn(C_6H_5)_3 + 2H_2O \]

Traces of benzoyl peroxide somewhat accelerate and traces of hydroquinone somewhat retard this reaction (see table).

We investigated also the course of the reaction of hydrotriphenyltin with halo hydrocarbons, acid chlorides, and metal halides. Hydrotriphenyltin reacts vigorously with carbon tetrachloride at room temperature with liberation of heat, which contrasts with the reaction of tributylgermane with carbon tetrachloride, which goes at 200° [5]. Reaction with chloroform is less vigorous, and butyl chloride does not react at all even at 100° for 12.5 h. Reaction of hydrotriphenyltin with benzochloride goes very vigorously at room temperature, benzylidene chloride reacts less vigorously, and benzyl chloride reacts at 80° with an 86% yield. Chlorobenzene and hydrotriphenyltin do not react when heated to 100° for 10.5 h, and at a higher temperature (135°) tetraphenyltin is formed; we isolated this substance, but in the main the starting compound was recovered unchanged.

Hence, with respect to the rate of the reaction between hydrotriphenyltin and organic halogen compounds the latter can be placed in the following order: \( \text{CCl}_4 > \text{RCCl}_3 > \text{RCHCl}_2 > \text{RCH}_2\text{Cl} > \text{CHCl}_3 \). The reactions of hydrotriphenyltin with acid chlorides go very smoothly with formation of chlorotriphenyltin and the corresponding aldehyde. We investigated the cases of acetyl and benzoyl chlorides. Hydrotriphenyltin reacts with metal halides with the liberation of the metal and the formation of hydrogen halide and hexaphenylditin:

\[ n(C_6H_5)_3SnH + MX_n \rightarrow [(C_6H_5)_3Sn - Sn(C_6H_5)_3]_{n/2} + nHX + M \]

This reaction was studied with \( \text{PCl}_3, \text{HgCl}_2, \) and \( \text{SbCl}_3 \). In a similar way triethylgermane reduces aluminum trichloride and germanium tetrachloride to aluminum and germanium, respectively [5]. In air, hydrotriphenyltin forms hexaphenylditin, and not tetraphenyltin [1], which is obtained when it is heated strongly.

EXPERIMENTAL

In all experiments we used hydrotriphenyltin of b.p. 170-172° (1 mm) and \( n_D^{20} 1.6362 \), prepared by the method given in [6]. All experiments were carried out under nitrogen.

Reaction of Hydrotriphenyltin with Oxygen. 1 g of hydrotriphenyltin was heated in oxygen for 8.5 h at 76-78°. We isolated 0.22 g of a white crystalline substance, which when recrystallized from benzene melted at 226-227°. A mixture with \( [(C_6H_5)_3Sn]_2 \) melted without depression. 0.75 g of hydrotriphenyltin was recovered unchanged.
Reaction of Hydrotriphenyltin with Oxygen in Presence of Benzoyl Peroxide. 1.5 g of hydrotriphenyltin was heated for 14.5 h at 76-78° in presence of benzoyl peroxide. We isolated 0.69 g of a white crystalline substance. After recrystallization from benzene it had m.p. 225-226°, undepressed by admixture with \([(C_6H_5)_3Sn]_2\). 0.75 g of unchanged hydrotriphenyltin was recovered.

Reaction of Hydrotriphenyltin with Oxygen in Presence of Hydroquinone. 1 g of hydrotriphenyltin was heated with oxygen for 8.5 h at 76-78° in presence of hydroquinone. We isolated 0.69 g of a white crystalline substance. After recrystallization from benzene it had m.p. 225-226°, undepressed by admixture with \([(C_6H_5)_3Sn]_2\). 0.84 g of hydrotriphenyltin was recovered unchanged.

Reaction of Hydrotriphenyltin with Carbon Tetrachloride. 1.04 g of hydrotriphenyltin was added at room temperature to 8 g of carbon tetrachloride. After a few minutes a vigorous reaction set in with liberation of heat. After one hour the excess of carbon tetrachloride was evaporated, and we then isolated 1.06 g (92.82%) of product. After being recrystallized from ethanol it melted at 103-104°. A mixture with known \((C_6H_5)_3SnCl\) melted without depression.

Reaction of Hydrotriphenyltin with Chloroform. 1.5 g of hydrotriphenyltin was added to 3.02 g of chloroform at room temperature. The mixture was heated for 5 h at 60°, and we then isolated 1.64 g (100%) of a white crystalline substance. After being recrystallized from ethanol it melted at 104-106°. A mixture with known \((C_6H_5)_3SnCl\) melted without depression.

Reaction of Hydrotriphenyltin with Butyl Chloride. 1.5 g of hydrotriphenyltin, n_D^20 1.6361, was added to 0.47 g of butyl chloride at room temperature. The mixture was heated at 73-76° for 10.5 h, and butyl chloride was removed. We isolated 1.5 g of hydrotriphenyltin unchanged. The experiment was then carried out in a sealed tube at 100° for 12.5 h: 1.5 g of unchanged hydrotriphenyltin, n_D^20 1.6364, was recovered.

Reaction of Hydrotriphenyltin with Chlorobenzene. 1.5 g of hydrotriphenyltin was added to 0.57 g of chlorobenzene at room temperature. The mixture was heated for 10.5 h at 100°, and the chlorobenzene was removed. By vacuum distillation of the residue in a stream of dry nitrogen we isolated 1.29 g of unchanged hydrotriphenyltin. In a second experiment the mixture was heated at 135° for 5.5 h. We isolated 0.08 g of a crystalline substance. After being recrystallized from benzene it melted at 224-226°. A mixture with \((C_6H_5)_3Sn\) melted without depression. Chlorobenzene was removed from the filtrate, and the residue (1.44 g, n_D^3 1.6340) consisted of unchanged hydrotriphenyltin.

Reaction of Hydrotriphenyltin with Acetyl Chloride. 1.5 g of hydrotriphenyltin was added to 1 g of acetyl chloride at room temperature. We isolated 0.81 g (49.17%) of a white crystalline substance. After recrystallization from ethanol it had m.p. 104-106°, undepressed by admixture of \((C_6H_5)_3SnCl\).