SYNTHESIS OF ORGANOTIN COMPOUNDS FROM ORGANOMERCURY COMPOUNDS AND STANNOUS SALTS IN INERT SOLVENTS

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In an investigation of the cis- and trans-propenyl compounds of lithium, thallium, and tin we attempted to effect the transfer of a propenyl group from a mercury atom to a tin atom by the method used in the synthesis of organotin compounds, as described by one of us and Kocheshkov [1]:

\[ \text{R}_2\text{Hg} + \text{SnX}_2 \rightarrow \text{R}_2\text{SnX}_2 + \text{Hg} \]

When we used alcohol or acetone as solvent, we did not succeed in isolating propenyltin compounds, though mercury was isolated almost quantitatively, as in the case of organomercury compounds containing "superaromatic" groups, for which reactions in solvents containing mobile hydrogen proceed in the direction of replacement of mercury by hydrogen and formation (in alcohol) of \((\text{C}_6\text{H}_5\text{O})_2\text{SnX}_2\). In spite of the extremely low solubility of stannous halides in hydrocarbons, it was found possible to carry out the reaction between stannous halides and dipropenylmercury in petroleum ether (and ligroin) and obtain stereoisomeric dipropenyltin dichlorides in yields of 70-75% [2].

The present communication is devoted to an investigation of the reaction of organomercury compounds with stannous salts in inert solvents with the object of establishing the limits to which this old method can be extended. We studied the reactions of the geometric isomers of dipropenylmercury [2], disisopropenylmercury, diethylmercury, diphenylmercury, di-p-tolylmercury, di-o-tolylmercury, and di-l-naphthylmercury with stannous bromide and chloride.

In the reaction of disisopropenylmercury with stannous bromide in petroleum ether at room temperature and at 65° we isolated disisopropenyltin dibromide (b. p. 102° (9 mm); \( n^\text{D} 1.5667 \)), tetraisopropenyltin (b. p. 65-66° (8 mm); \( n^\text{D} 1.5110 \)), isopropenylmercury bromide, and mercury. The geometric isomers of dipropenylmercury react with stannous bromide with formation of only dipropenyltin dibromide and mercury [2].

Among the products of reaction between diethylmercury and stannous chloride we found diethyltin dichloride and ethylmercury chloride.

In the reaction of diphenylmercury with stannous chloride at various temperatures we always obtained only triphenyltin chloride, which was evidently formed via \((\text{C}_6\text{H}_5)_2\text{SnCl}_2\), as follows:

\[ 2(\text{C}_6\text{H}_5)_2\text{SnCl}_2 + \text{Hg}(\text{C}_6\text{H}_5)_2 \rightarrow 2(\text{C}_6\text{H}_5)_2\text{SnCl} + \text{HgCl}_2 \]

The reaction with stannous bromide proceeds similarly, but the yield of triphenyltin bromide is lower.

Di-p- and di-o-tolylmercurys react with stannous chloride with formation of only the corresponding ditolyltin dichlorides, and no toluene has been detected among the reaction products [1]. Reaction of di-l-naphthylmercury with stannous chloride gives only di-l-naphthyltin dichloride. Attempts to synthesise aromatic tin compounds containing substituents such as OH and \( \text{N}(\text{CH}_3)_2 \) in the benzene nucleus were not successful. In
the products of the reaction of bis-o-hydroxyphenylmercury with stannous chloride the presence of a small amount of phenol was established, but no reactions occurred with (p-dimethylaminophenyl)mercury chloride and with dibenzylmercury.

Experimental

Reaction of Diisopropenylmercury with Stannous Bromide

A. A mixture of 5.9 g (0.02 mole) of diisopropenylmercury and 12 g (0.04 mole) of stannous bromide in 30 ml of petroleum ether (b. p. 60-70°) was stirred vigorously for five hours at room temperature. After one hour the solution was decanted, and the precipitate was washed three times with petroleum ether and then with acetone. Evaporation of the acetone solution gave 1.72 g of isopropenylmercury bromide, m. p. 165-167°. After evaporation of petroleum ether there remained a liquid, which was treated with 30 ml of 20% KOH solution; the precipitate then formed was separated and treated with 15% hydrobromic acid solution. From the reaction products we isolated 1.7 g (22%; of theor.) found MR 60.84; calculated MR 60.88.

Found %: C 19.64, 19.78; H 2.70, 2.81; Sn 32.62, 33.00. C6H10SnBr2. Calculated %: C 19.98; H 2.79; Sn 32.91.

The alkaline solution was extracted with ether, the extract was dried, solvent was distilled off from a water bath, and the residue was distilled. We collected 0.6 g of tetraisopropenyltin b. p. 66-67° (8 mm); nD 1.5110; d4 1.3153; found MR 64.43; 0.6 g.

Found %: Sn 42.11, 42.40. C12H26Sn. Calculated %: Sn 41.95.

We isolated 1.86 g (44%; of mercury.

B. A mixture of 4 g (0.014 mole) of diisopropenylmercury and 8 g (0.028 mole) of stannous bromide in 20 ml of petroleum ether was stirred for five hours at 65°. The reaction products were isolated as in experiment A. We obtained 1.03 g of isopropenylmercury bromide, m. p. 165-167°, 1.1 g (21%) of diisopropenyltin dibromide, nD 1.5110; d4 1.3153; found MR 64.43; 0.6 g.

Found %: C 19.64, 19.78; H 2.70, 2.81; Sn 32.62, 33.00. C6H10SnBr2. Calculated %: C 19.98; H 2.79; Sn 32.91.

C. To 1 g (0.0035 mole) of diisopropenylmercury in 5 ml of acetone we added 2 g (0.007 mole) of stannous bromide in 10 ml of acetone. The reaction mixture was allowed to stand for 20 hours and then treated as in experiment A. We obtained 0.57 g of tetraisopropenyltin, b. p. 66-67° (8 mm); nD 1.5110; d4 1.3153; found MR 64.43; 0.6 g.

Found %: C 19.64, 19.78; H 2.70, 2.81; Sn 32.62, 33.00. C6H10SnBr2. Calculated %: C 19.98; H 2.79; Sn 32.91.

We isolated 1.86 g (44%) of mercury.

Reaction of Diethylmercury with Stannous Chloride

A mixture of 5 g (0.019 mole) of diethylmercury and 7 g (0.036 mole) of stannous chloride in 25 ml of ligroin (b. p. 100-110°) was stirred vigorously at 85-90° for 12 hours. The cooled solution was decanted, and the precipitate was extracted three times with warm petroleum ether and then with methanol. After evaporation of the petroleum ether we isolated 2.5 g (52%) of diethyltin dichloride, which after recrystallization from petroleum ether had m. p. 83-83.5° (82-84° [1]). From the methanol solution we obtained 1 g of ethylmercury chloride, m. p. 191-192°. We isolated 2.59 g (69%) of mercury.

Reaction of Diphenylmercury with Stannous Chloride

A mixture of finely divided diphenylmercury (3 g, 0.0084 mole) and stannous chloride (3 g, 0.16 mole) in 50 ml of dry ligroin was stirred vigorously for seven hours at 60-65°. We separated 1.66 g (98.2%) of mercury. Part of the solvent was distilled from the filtrate, and we isolated 1.65 g (75%) of crystalline triphenyltin chloride, m. p. 94-97°, raised to 102-104° by recrystallization from petroleum ether.

Found %: C 55.46; H 3.88, 3.91; Sn 30.85; 30.63. C18H18SnCl. Calculated %: C 56.07; H 3.89; Sn 30.81.

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