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Abstract

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SYNTHESIS OF ORGANOTIN COMPOUNDS THROUGH DOUBLE IODONIUM SALTS

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There are a few data in the literature on the use of diaryliodonium salts as starting substances for the synthesis of organometallic compounds. Thus, Sandin, McClure, and Irwin ([1]), decomposing diphenyliodonium chloride* with mercury and tellurium in propyl alcohol and with antimony in water in the presence of Na_2S, obtained the corresponding organoelement compounds. However, the authors indicate the yield only for phenylmercury chloride. L. G. Makarova and A. N. Nesmeyanov ([2]) used iodonium salts for arylation of organoelement compounds. On thermal decomposition of $(C_6H_5)_2J^+BF_4^-$ in the presence of substances of the type Ar_n (where $= \mathrm{Sb, As, Bi, P, Se}$), they obtained the corresponding onium organoelement compounds.

We found that, upon decomposition by metal powders of double salts of diaryliodonium chloride and heavy-metal chlorides,** the corresponding organometallic compounds are formed.

The present article describes the synthesis of organotin compounds through double iodonium salts of tin chloride:

$$2\mathrm{Ar_2JCl \cdot SnCl_2 + Sn \rightarrow Ar_2SnCl_2 + 2ArJ + 2SnCl_2}.$$

It should be noted that, for obtaining organotin compounds, there is no need to prepare double iodonium salts, since we have shown that diphenylstannane oxide is obtained both upon decomposition of $Ar_2JCl \cdot SnCl_2$ and upon decomposition of a mixture of Ar_2JCl and $SnCl_2$ with tin powder. That in the latter case the reaction proceeds through the stage of double iodonium salts follows, first, from the fact that diaryliodonium chlorides, poorly soluble in acetone, dissolve upon addition of $SnCl_2$, and, second, from the fact that Ar_2JCl under the reaction conditions is not decomposed by tin powder and gives no organotin compounds.

The compounds synthesized by the above method are given in Table 1 (for comparison, the yields of organotin compounds achieved by the Nesmeyanov diazo method ([4],[5]) are given).

As can be seen from Table 1, the yields of organotin compounds obtained by the method of double iodonium salts considerably exceed the yields achieved by the Nesmeyanov diazo method. This circumstance, along with the simplicity of carrying out the synthesis, makes it possible to regard the proposed method as a convenient route for obtaining aromatic organotin compounds***.

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* Along with $(C_6H_5)_2JCl$, the same authors decomposed $(n\text{-}C_7H_7)_2JCl$ with mercury and tellurium in propyl alcohol, but the yields of the corresponding organoelement compounds are not given.

** Double salts of diaryliodonium chloride with $HgCl_2$, $AuCl_3$, and $PtCl_4$ have long been known (^{3}). We obtained double salts with $SnCl_2$, $SnCl_4$, $SbCl_3$, $SbCl_5$, and $BiCl_3$ by mixing hydrochloric-acid solutions of Ar_2JCl and the chlorides of the corresponding metals.

*** It should be noted that, by an analogous route, organometallic compounds of other metals (Hg, Sb, Bi) are formed from double iodonium salts.

Table 1

Reaction products*	Yield, % via double iodonium salts	Yield, % by Nesmeyanov' s diazo method: via double diazonium salts	Yield, % by Nesmeyanov' s diazo method: via aryldiazonium borofluorides**
$(C_6H_5)_2SnO$	76	23	43
$(n\text{-}C_7H_7)_2SnO$	67	–	38.4
$(n\text{-}ClC_6H_4)_2SnO$	82	4.7	21
$(n\text{-}BrC_6H_4)_2SnO$	47	6	30.2
$(n\text{-}JC_6H_4)_2SnO$	39	–	–

* All the substances obtained were identified in the form of the corresponding halides. For this purpose, a solution of diaryltin oxide in glacial acetic acid was poured into cooled, dilute hydrohalic acid; the precipitated halide was filtered off and recrystallized.
** The total yield of organotin compounds is given.

Experimental Part

1. Synthesis of diphenyltin oxide. 20 g (0.063 M) of $(C_6H_5)_2JCl$ was introduced into 25 ml of acetone, and then, with vigorous stirring, 20 g (0.1 M) of anhydrous $SnCl_2$ and 10 g (0.084 g-atom) of tin powder were added. After some time the reaction mass warmed almost to boiling. After vigorous stirring for 4 hours, the inorganic precipitate was filtered off and the solvent was evaporated. The oil remaining after evaporation of the acetone was washed with HCl (1 : 1), dissolved in alcohol, and the alcoholic solution was poured in the cold into a 10% NaOH solution. The precipitated diphenyltin oxide was filtered off, washed with water, alcohol, and ether. Yield 7 g (76% of theory).

Found, %: Sn 41.14; 41.20; C 49.66; 49.90; H 3.79; 3.95
$(C_6H_5)_2SnO$. Calculated, %: Sn 41.08; C 49.87; H 3.49

2. Synthesis of di-*n*-tolyltin oxide. 7 g (0.02 M) of $(n\text{-}C_7H_7)_2JCl$ and 4 g (0.002 M) of anhydrous $SnCl_2$ in 20 ml of acetone were decomposed with 3 g (0.025 g-atom) of tin. The reaction mixture was stirred for 2 hours. As a result of work-up analogous to the preceding experiment, 2.15 g of di-*n*-tolyltin oxide (67% of theory) was isolated. $(n\text{-}C_7H_7)_2SnO$ was converted into di-*n*-tolyltin bromide*. After recrystallization from petroleum ether, m.p. 74°. Literature data (6): m.p. 74°.

Found, %: C 36.20; 36.41; H 3.05; 3.04
$(C_7H_7)_2SnO$. Calculated, %: C 36.49; H 3.06

3. Synthesis of di-*n*-chlorophenyltin oxide. 19 g (0.05 M) of $(n\text{-}ClC_6H_4)_2JCl$ and 9.5 g (0.05 M) of anhydrous $SnCl_2$ in 25 ml of acetone were decomposed with 6 g (0.05 g-atom) of tin. After work-up, 7.25 g of di-*n*-chlorophenyltin oxide (82% of theory) was isolated, identified in the form of $(n\text{-}ClC_6H_4)_2SnCl_2$. M.p. 88°. Literature data (7): m.p. 86.5°.

Found, %: C 35.04; 35.02; H 2.07; 1.91
$(ClC_6H_4)_2SnCl_2$. Calculated, %: C 34.92; H 1.95

4. Synthesis of di-*n*-bromophenyltin oxide. 4 g (0.084 M) of $(n\text{-}BrC_6H_4)_2JCl$ and 2 g (0.01 M) of anhydrous $SnCl_2$ were decomposed with 1.5 g (0.013 g-atom) tin powder under the conditions of the preceding experiment. The mass remaining after evaporation of the solvent was extracted with benzene, the benzene was evaporated, and alcohol was added to the residue. The alcoholic solution was hydrolyzed with 10% NaOH. The precipitated di-*p*-bromophenyltin oxide was filtered off and washed with alcohol and ether. Yield 1 g (47% of theory). $(p\text{-}BrC_6H_4)_2SnO$ was identified in the form of $(p\text{-}BrC_6H_4)_2SnCl_2$. M.p. 104°. Literature data [7]: m.p. 103°.

Found, %:	C 29.11; 28.91;	H 1.84; 1.79
$(BrC_6H_4)_2SnCl_2$. Calculated, %:	C 28.74;	H 1.61

5. Synthesis of di-*p*-iodophenyltin oxide. 11.4 g (0.02 M) of $(p\text{-}JC_6H_4)_2JCl$ and 4 g (0.02 M) of anhydrous $SnCl_2$ were decomposed by 3 g (0.025 g-at.) of tin powder in 20 ml of acetone. As a result of treatment analogous to that in the preceding experiment, 2.1 g of di-*p*-iodophenyltin oxide (39% of theory)

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* In this case di-*n*-tolyltin bromide was obtained, and not $(n\text{-}C_7H_7)_2SnCl_2$, since the latter precipitated as an oil.

was isolated, identified in the form of di-*p*-iodophenyltin dichloride. M.p. 147°. Literature data [7]: m.p. 147°.

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Note: Figure translations are in progress. See original paper for figures.