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## Abstract

## Full Text

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# SYNTHESIS OF ORGANOMERCURY COMPOUNDS VIA DIARYLIODONIUM SALTS

As we have shown earlier ([1,2]), double salts of diaryliodonium chlorides and metal chlorides can serve as a source for obtaining organometallic compounds of tin, antimony, and bismuth. The reaction consists in the decomposition of double diaryliodonium salts by powders of tin, antimony, and bismuth, respectively.

In the present work, the possibility of extending this reaction to the synthesis of organomercury compounds has been studied. In order to find the optimum conditions, we decomposed the double salt of diphenyliodonium chloride and mercuric chloride in various solvents, using a series of metals (Hg, Fe, Zn, Cu, Ag) as reducing agents. The results of these experiments are given in Table 1.

**Table 1**

Yield of the organomercury compound (in percent) for various metal reducing agents

| Solvent | Hg | Fe | Zn | Cu | Ag |
|---|---|---|---|---|---|
| Water | 70 | — | — | — | — |
| Acetone | 34 | 3 (39)* | 30 | 16 | 0 |
| Ethyl alcohol | — | 5 (21)* | traces | 9 | — |

* The yield of diphenylmercury is indicated in parentheses.

As can be seen from Table 1, when iron was used as the metal reducing agent, the main reaction product was diphenylmercury; in the other cases it was $C_6H_5HgCl$. Silver decomposes the double salt $(C_6H_5)_2JCl \cdot HgCl_2$ with formation of diphenyliodonium chloride and calomel; in this case organomercury compounds are not formed. The maximum yield of phenylmercuric chloride is achieved when the double salt of diphenyliodonium chloride and mercuric chloride is decomposed by mercury in water

$$(C_6H_5)_2JCl \cdot HgCl_2 + Hg \rightarrow C_6H_5HgCl + C_6H_5J + HgCl_2.$$

Decomposition under analogous conditions of $(n\text{-}ClC_6H_4)_2JCl \cdot HgCl_2$ and $(n\text{-}CH_3OC_6H_4)_2JCl \cdot HgCl_2$ led to the formation of *n*-chlorophenylmercuric chloride (yield 45%) and *n*-anisylmercuric chloride (yield 28%), respectively.

Thus, through double diaryliodonium salts of mercuric chloride, organomercury compounds are obtained in high yield only in the case of $(C_6H_5)_2JCl \cdot HgCl_2$. In addition, in the synthesis of organomercury compounds via $Ar_2JCl \cdot HgCl_2$, it is necessary first to obtain the initial double diaryliodonium salts, which in a number of cases are formed with difficulty owing to the low solubility of $Ar_2JCl$. The latter circumstance is a particularly significant obstacle to the broad application

double diaryliodonium salts with $HgCl_2$ for the synthesis of organomercury compounds. Therefore, in the subsequent work we decided to use diphenyliodonium salts directly as starting substances for obtaining organometallic compounds of mercury.

There are references in the literature to the use of diaryliodonium salts for the synthesis of organomercury compounds. Thus, Sandin, McClure, and Irwin ([3]) obtained $C_6H_5HgCl$ and *p*-$CH_3C_6H_4HgCl$ by decomposition of the chlorides of the corresponding diaryliodoniums with mercury in boiling propyl alcohol. The yield is given only for phenylmercury chloride (40%). L. G. Makarova and A. N. Nesmeyanov ([4]), repeating the experiment of Sandin and co-workers, obtained $C_6H_5HgCl$ in a yield of 50%.

In view of the fact that the few data currently available on the use of diaryliodonium salts for obtaining organomercury compounds are only of an orienting character, we undertook a detailed study of the possibility of synthesizing organomercury compounds through diaryliodonium salts. The results of the decomposition of diphenyliodonium chloride by metallic mercury in various solvents are given in Table 2.

Table 2

| Solvent | Yield of $C_6H_5HgCl$, % |
|---|---|
| Acetone | 76 |
| Benzene | 50 |
| Water | 34 |
| Propyl alcohol ([3]) | 40 |

As can be seen from Table 2, the most favorable solvent is acetone, in which the reaction was usually carried out in the following manner. Diaryliodonium chloride (0.01 mole) was vigorously stirred with 2 ml of mercury in 100 ml of acetone for 3 h at 56°. The precipitate was filtered off and extracted with acetone; the extract was combined with the filtrate. The resulting solution was evaporated. The remaining organomercury compound was freed from the corresponding iodine derivative, formed in the course of the reaction, by washing with

hot petroleum ether. After recrystallization, an analytically pure organomercury compound was obtained. The compounds synthesized by the indicated method are given in Table 3.

Table 3

| Starting diaryliodonium salt | Reaction product | Yield, % |
|---|---|---|
| $(C_6H_5)_2JCl$ | $C_6H_5HgCl$ | 76 |
| $(n\text{-}CH_3C_6H_4)_2JCl$ | $n\text{-}CH_3C_6H_4HgCl$ | 55 |
| $(n\text{-}CH_3OC_6H_4)_2JCl$ | $n\text{-}CH_3OC_6H_4HgCl$ | 53 |
| $(n\text{-}ClC_6H_4)_2JCl$ | $n\text{-}ClC_6H_4HgCl$ | 77 |
| $(n\text{-}BrC_6H_4)_2JCl$ | $n\text{-}BrC_6H_4HgCl$ | 75 |
| $(m\text{-}O_2NC_6H_4)_2JCl$ | $m\text{-}O_2NC_6H_4HgCl$ | 40 |
| $(m\text{-}C_2H_5OCOC_6H_4)_2JCl$ | $m\text{-}C_2H_5OCOC_6H_4HgCl$ | 47 |

As can be seen from Table 3, organomercury compounds are obtained through diaryliodonium salts in good yield. This circumstance, as well as the simplicity of carrying out the synthesis and the comparative accessibility of diaryliodonium salts, makes it possible to regard the proposed synthesis method as a convenient route for obtaining organomercury compounds.

It should be noted that, in addition to symmetrical diaryliodonium salts, we decomposed three unsymmetrical salts: $C_6H_5(n\text{-}CH_3OC_6H_4)JCl$, $(n\text{-}CH_3OC_6H_4)(n\text{-}C_2H_5OCOC_6H_4)JCl$, and $C_6H_5(n\text{-}JC_6H_4)JCl$. In the first two cases, $C_6H_5HgCl$ (yield 70%) and $n\text{-}C_2H_5OCOC_6H_4HgCl$ (yield 56%), respectively, were obtained, i.e., of the two radicals the more electronegative passed to the mercury. Transfer of the more electronegative radical was also observed by us in the decomposition of the double salt $C_6H_5(n\text{-}CH_3OC_6H_4)JCl \cdot HgCl_2$ by iron powder. Here, as in the decom-

decomposition of the double salt of chlorodiphenyliodonium and sublimate, the main product was diphenylmercury (yield 29%), along with traces of phenylmercuric chloride. Decomposition of $C_6H_5(n\text{-}JC_6H_4)JCl$ by mercury, however, leads to the formation of a mixture of products: $C_6H_5HgCl$ and $n\text{-}JC_6H_4HgCl$, i.e., in this case

$$2\,\begin{matrix}C_6H_5\\CH_3O\,C_6H_4\end{matrix}JCl \cdot HgCl_2 + 2Fe \longrightarrow$$

$$\longrightarrow C_6H_5{-}Hg{-}C_6H_4OCH_3 + 2CH_3O{-}C_6H_4{-}J + 2FeCl_2 + Hg.$$

both radicals pass onto mercury. This is probably explained by the fact that the difference in electronegativity of the phenyl and *n*-iodophenyl radicals is not as great as in the two preceding cases.

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## CITED LITERATURE

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