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Abstract

Full Text

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DECOMPOSITION OF UNSYMMETRICAL DIARYLIODONIUM SALTS BY BISMUTH POWDER IN THE PRESENCE OF BISMUTH TRICHLORIDE

It was found earlier (^{1}) that, in the decomposition of diaryliodonium chlorides by tin powder in the presence of stannous chloride, organotin compounds are formed in good yields. It was subsequently shown that, in the decomposition under these conditions of unsymmetrical diaryliodonium salts of the type $ArAr'JCl$, the more electronegative radical passes from iodine to tin. All these reactions evidently proceed through the preliminary stage of formation of double iodonium salts of stannous chloride, which are also decomposed by tin powder.

The present paper describes the results of the decomposition of unsymmetrical diaryliodonium salts by metallic bismuth powder in the presence of bismuth trichloride. In (^{1}) the possibility was shown of forming organobismuth compounds in the decomposition of double salts of diaryliodonium chlorides and bismuth trichloride by elemental bismuth powder. From the preparative standpoint it proved more convenient to decompose with bismuth not the double salt, but a mixture of Ar_2JCl and $BiCl_3$. Under these conditions the yield, for example, of triphenylbismuth reaches 35-40%.

The decomposition of unsymmetrical diaryliodonium salts* was carried out under conditions that proved optimal for obtaining triphenylbismuth through iodonium salts, namely: a mixture of the iodonium salt and $BiCl_3$ was decomposed by bismuth powder in acetone, with vigorous stirring, at room temperature**. After completion of the reaction the precipitate was filtered off, and the filtrate was poured into an ammonia solution. Under such treatment the mono- and diarylbismuth organic compounds, which are probably the initial reaction products, were converted into triaryl compounds. The reactions taking place may be expressed by the following equations:

$$3ArBiCl_2 \rightleftharpoons Ar_3Bi + 2BiCl_3$$

$$3\mathrm{Ar_2BiCl} \rightleftharpoons 2\mathrm{Ar_3Bi} + \mathrm{BiCl_3}$$

$$\mathrm{BiCl_3} + 3\mathrm{NH_4OH} \longrightarrow \mathrm{Bi(OH)_3} + 3\mathrm{NH_4Cl}$$

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* We note that the unsymmetrical iodonium salts were obtained by condensation of the corresponding iodoso compound with the hydrocarbon under the action of sulfuric acid in an acetic-acid medium. For the synthesis of the iodoso compounds we used the method, described in the literature, of oxidation of iodo derivatives with peracetic acid ([2],[3]). The iodoso compounds formed were not isolated, but were immediately introduced into the condensation. Thus, the synthesis of unsymmetrical iodonium salts was carried out in one stage. By this method the following salts were obtained:

$$\mathrm{C_6H_5}(n\text{-}\mathrm{CH_3OC_6H_4})\mathrm{JCl}$$

(yield 76%, m.p. 181°),

$$\mathrm{C_6H_5}(n\text{-}\mathrm{ClC_6H_4})\mathrm{JCl}$$

(yield 70%, m.p. 196°),

$$\mathrm{C_6H_5}(n\text{-}\mathrm{BrC_6H_4})\mathrm{JCl}$$

(yield 80%, m.p. 193°),

$$(n\text{-}\mathrm{CH_3OC_6H_4})(n\text{-}\mathrm{C_2H_5OCOC_6H_4})\mathrm{JCl}$$

(yield 54%, m.p. 150°).

** When the reaction was carried out in boiling acetone or absolute alcohol, the yield of the organobismuth compound remained practically unchanged.

To separate triarylbismuth from inorganic bismuth compounds, the precipitate that had fallen out from ammonia was filtered off (after standing overnight), dried in air, and extracted with ether. Together with $\mathrm{Ar_3Bi}$, the corresponding iodine derivative of the aromatic series, which is formed upon decomposition of diaryliodonium salts according to the equation, also passed into the ethereal solution:

$$3\,\begin{matrix}\mathrm{Ar}\\ \mathrm{Ar'}\end{matrix}\!>\mathrm{JCl} + 2\mathrm{Bi} \xrightarrow{(\mathrm{BiCl_3})} \mathrm{Ar_3Bi} + 3\mathrm{Ar'J} + \mathrm{BiCl_3}$$

The iodine derivative was separated from triarylbismuth by steam distillation.

The unsymmetrical diaryliodonium salts decomposed by the method described above, and the substances obtained thereby, are listed in Table 1.

As is seen from Table 1, in all cases the more electronegative radical is transferred to bismuth. In not a single case were we able to isolate the second product, although it is quite probable that, in the decomposition of unsymmetrical iodonium salts in which the difference in electronegativity of the radicals is small, simultaneous transfer to bismuth of the less electronegative radical is possible. However, the second substance is evidently formed in such insignificant amounts that it can be detected only by some physicochemical methods, for example, by chromatography.

Table 1

Initial diaryliodonium salt	Reaction product	Yield, %
$\begin{matrix} n\text{-}ClC_6H_4 \\ C_6H_5 \end{matrix} > JCl$	$(n\text{-}ClC_6H_4)_3Bi$	13
$\begin{matrix} n\text{-}BrC_6H_4 \\ C_6H_5 \end{matrix} > JCl$	$(n\text{-}BrC_6H_4)_3Bi$	16
$\begin{matrix} n\text{-}CH_3OC_6H_4 \\ C_6H_5 \end{matrix} > JCl$	$(C_6H_5)_3Bi$	23
$\begin{matrix} n\text{-}CH_3OC_6H_4 \\ n\text{-}ClC_6H_4 \end{matrix} > JCl$	$(n\text{-}ClC_6H_4)_3Bi$	19

In view of the fact that the magnitude of the electron density is not the determining factor in radical reactions (^{4}), the results obtained by us are difficult to understand if one assumes that decomposition of the double iodonium salts proceeds homolytically. At the same time, the regularity we observed—that, upon decomposition of unsymmetrical iodonium salts, the more electronegative radical is transferred to the metal—can easily be explained by assuming heterolytic decomposition of the double iodonium salts. Then, for example, the formation of an organobismuth compound upon decomposition of phenyliodonium *p*-anisyl chloride may be represented as follows:

$$[C_6H_5{-}J^+{-}C_6H_4OCH_3]\,[BiCl_4]^- \longrightarrow [C_6H_5 \cdots J^+{-}C_6H_4OCH_3]\ BiCl_2{}^- \quad (A) \longrightarrow C_6H_5BiCl_2 + CH_3O{-}C_6H_4{-}J$$

Since the methoxyl group has electron-donor properties, there is a partial negative charge on the carbon atom bonded to the iodine atom. As a result, the bond of the positively charged iodine with the anisyl radical becomes stronger.

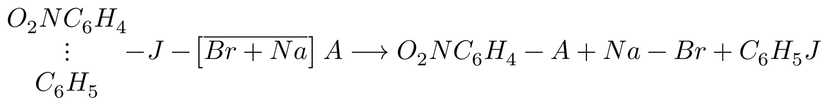
The carbon atom of the phenyl radical bonded to iodine is a site of comparatively lower electron density. Therefore its bond with iodine is not as strong as the bond of the anisyl radical. Detachment of phenyl in the form of a cation and transfer to the negatively charged (in the intermediate ···)

in complex A) the bismuth atom is more probable than the anisyl group. This, apparently, is the reason for the formation of organobismuth compounds with more electronegative radicals. The data obtained by Beringer and co-workers (5) support the proposed heterolytic character of the decomposition under consideration of unsymmetrical iodonium salts. They studied the interaction of unsymmetrical iodonium salts

$$[(o\text{-}O_2NC_6H_4)C_6H_5J]Br \quad \text{and} \quad [(m\text{-}O_2NC_6H_4)C_6H_5J]Br$$

with $NaNO_2$, $NaOH$, $NaCN$, CH_3ONa, etc.

All these definitely heterolytic reactions can, in general form, be represented by the following equation:



$$\begin{matrix} O_2NC_6H_4 \\ \vdots \\ C_6H_5 \end{matrix} -J-\left[\overline{Br+Na}\right] A \longrightarrow O_2NC_6H_4-A+Na-Br+C_6H_5J$$

The anion A^-, as also in our cases, always receives the more electronegative radical.

It is interesting to note that in the thermal decomposition of iodonium salts, proceeding homolytically (6), a mixture of products is formed, for example:

$$\text{[scheme: } (p\text{-}CH_3OC_6H_4)(C_6H_5)JCl \longrightarrow CH_3OC_6H_4J + C_6H_5Cl$$
$$\text{and } CH_3OC_6H_4Cl + C_6H_5J\text{]}$$

i.e., in this case the polar factor does not play a noticeable role.

Despite the fact that recently more and more information has appeared indicating the known role of polar factors in radical reactions, the totality of the data set forth by us supports a heterolytic mechanism for the reactions considered by us of decomposition of double iodonium salts*.

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* The fact that the reactions studied by us of the decomposition of diaryliodonium chlorides by metal powders proceed through the stage of double diaryliodonium salts is also evidenced by a number of facts. One of them is, for example, the formation of triphenylbismuth upon decomposition by copper of the double salt of chlorodiphenyliodonium and bismuth trichloride. Since copper cannot displace Bi from $BiCl_3$, the formation of $(C_6H_5)_3Bi$ otherwise than through the stage of a double iodonium salt is difficult to imagine.

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.