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Abstract

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SYNTHESIS OF SOME ORGANOELEMENT DERIVATIVES OF POLYVALENT ASTATINE

(Presented by Academician A. N. Nesmeyanov, January 15, 1962)

The ability to form organic derivatives of definite composition and structure is one of the important characteristics of an element. The exceptional progress that has been observed in recent years in the chemistry of organoelement derivatives as a whole has not at all affected such typically radioactive elements as francium and astatine. At the same time, the ability of these elements to give organoelement compounds undoubtedly follows from their position in the periodic system, as well as from the general regularities of formation and stability of organoelement compounds ([1,2]). Certain successes have been achieved only in the chemistry of organic derivatives of another typically radioactive element –polonium ([3–6]). These successes are connected mainly with the development of new methods of synthesis based on the processes of stabilization and decay of molecular ions arising as a result of β-transitions.

The information available in the world literature on the chemistry of organoelement compounds of astatine is limited only to indications of the existence of astatobenzene and astatophenol*. These indications are based on data from experiments on the reextraction of astatine from certain organic solvents ([7,8]).

The aim of the present work was to obtain organoelement derivatives of polyvalent astatine by classical methods of synthesis. In doing so we proceeded from the assumption that the ability, characteristic of iodine (and distinguishing it from other halogens), to form organic derivatives of higher valence states should be even more pronounced in astatine.

Most organoiodine derivatives contain iodine atoms in the trivalent state. Compounds of this type include organic iododihalides, as well as iodoso and iodonium compounds. Organic derivatives with pentavalent iodine are represented by the group of iodoxy compounds ([6,7]). Table 1 gives the valence groups and absolute valences of the indicated types of compounds. The symbol (2) denotes an inert electron pair.

Fig. 1

Figure 1: Fig. 1

Experimental Part

Syntheses of organic compounds of polyvalent astatine were carried out by methods described in the literature for analogous iodine compounds ([6,10]), with certain modifications, mainly connected with the necessity of shortening the synthesis time because of the comparatively short half-lives of astatine isotopes (the half-lives for the isotopes At^{210} and At^{211} are, respectively, 8.3 and 7.5 hours) ([11]).

The indicated astatine isotopes were obtained on the synchrophasotron of the Joint Institute for Nuclear Research by the reaction of deep spalla-

* It should also be noted that there are some patent works on the preparation of biological preparations containing astatine ([14,15]).

···during irradiation of thorium with protons of energy 660 MeV. Astatine was isolated from the target by the method described in (12), followed by chromatographic concentration (13). Syntheses of organoelement compounds of astatine were carried out using as the nonisotopic carrier its closest analogue—iodine.

Fig. 1. Chromatographic behavior of $PhJ(At)Cl_2$ (a) and of a mixture of $PhJ(At)Cl_2$ + $Ph_2J(At)Cl$ (b) upon development in acetone. 1 —$PhAtCl_2$, 2 — $PhJCl_2$, 3 —Ph_2AtCl + $PhAtCl_2$, 4 —Ph_2JCl + $PhJCl_2$.

As preliminary studies with organoiodine compounds showed, the most expedient scheme for the synthesis of organoastatine compounds is the following:

$$Ph_2JCl + KJ(At) \rightarrow Ph_2JJ(At) \xrightarrow{170^\circ} PhJ(At) \xrightarrow{Cl_2} Ph_2J(At)Cl$$

$$\rightarrow PhJ(At)Cl_2 \begin{array}{l} \xrightarrow{Ph_2Hg} Ph_2J(At)Cl \\ \xrightarrow{NaOCl} PhJ(At)O_2 \end{array}$$

Separation and identification of organoelement compounds of astatine were carried out by paper chromatography. In doing so, we proceeded from the identity of properties and, consequently, from the assumption of identity in the chromatographic behavior of analogous compounds of astatine and iodine. The chromatographic behavior of compounds of the latter was studied with the aid of the corresponding compounds labeled with a radioactive isotope of iodine.

Synthesis of $PhAtCl_2$. To an aqueous solution of diphenyliodonium chloride placed in a glass ampoule, a solution of KJ(At)* was added; the crystalline precipitate that formed was centrifuged and washed with a small amount of

Figure 2

Figure 2: Figure 2

alcohol. The ampoule was sealed and heated for 5 min at 170°. Under these conditions $Ph_2J \cdot J(At)$ decomposed according to the scheme:

$$Ph_2J \cdot J(At) \rightarrow 2PhJ(At).$$

A small amount of chloroform was added to the reaction product, and after cooling to 0° PhJ(At) was chlorinated until the separation of a yellow crystalline precipitate of $PhJ(At)Cl_2$ ceased. The precipitate was recrystallized from a small amount of chloroform. The chloroform solution was applied to a strip of chromatographic paper ("fast"), and after removal of the solvent chromatography was carried out using as–

* To convert chloride complexes of astatine, in the form in which it is obtained after chromatographic concentration, into the KAt form, a calculated amount of potassium iodide was added to the solution and the astatine was reduced with sulfurous gas.

as the developing solvent–acetone. The chromatograms obtained are presented in Fig. 1, in which, for comparison, chromatograms of analogous iodine compounds are given. As follows from the figure, the positions of the peaks of β-active chloroiodobenzene and of the α-active astatine peaks coincide. Hence it may be concluded that astatine is present in the form of the analogous compound $PhAtCl_2$.

This conclusion is confirmed by experiments on repeated recrystallization of crystals of $PhJ(At)Cl_2$, which showed that the specific activity of this compound practically retains its value even after sixfold recrystallization*.

Fig. 2. Chromatographic behavior of $PhJ(At)Cl_2$ when developed in acetone (aqueous phase after separation of $PhJ(At)Cl_2 + Ph_2J(At)Cl$). 1 –$PhAtO_2$, 2 –$PhJO_2$

Synthesis of Ph_2AtCl. To obtain $Ph_2J(At)Cl$, $PhJ(At)Cl_2$ was used. The crystals were dissolved in chloroform, the solution was heated to boiling, and a hot chloroform solution of diphenylmercury was slowly added to it. The mixture was heated for several minutes on a water bath and then cooled. The precipitate that separated was centrifuged off. The reaction proceeded according to the scheme:

$$PhJ(At)Cl_2 + HgPh_2 \rightarrow Ph_2J(At)Cl + HgPhC.$$

$$PhJ(At)Cl_2 + HgPhCl \rightarrow Ph_2J(At)Cl + HgCl_2.$$

Figure 3

Figure 3: Figure 3

Fig. 4. Chromatographic behavior of $PhJ(At)O_2$ upon development in acetone. 1 –Ph_2AtCl, 2 –Ph_2JCl

Figure 4: Fig. 4. Chromatographic behavior of $PhJ(At)O_2$ upon development in acetone. 1 –Ph_2AtCl, 2 –Ph_2JCl

The mixture remaining in solution, $PhJ(At)Cl_2$ + $Ph_2J(At)Cl$, was subjected to chromatographic separation. The chromatograms obtained are presented in Fig. 1b, from which the coincidence of the β- and α-active peaks of the corresponding iodine and astatine derivatives is visible.

Fig. 3. Chromatographic behavior of $Ph_2J(At)Cl$ when developed in acetone (chloroform phase after separation of $PhJ(At)Cl_2$ and $Ph_2J(At)Cl$). 1 –$PhAtCl_2$, 2 –$PhJCl_2$.

For further identification of $Ph_2J(At)Cl$, it was separated from the starting substance $PhJ(At)Cl_2$, followed by chromatography of the separated products. The separation was based on the ability of iodonium derivatives to be extracted from organic solvents by water. The results of chromatography of the aqueous and chloroform phases are presented in Figs. 2 and 3. The position of the α-active astatine peaks coincides with the position of the β-peaks of the corresponding organoiodine compounds.

Synthesis of $PhAtO_2$. As is seen from the scheme for the synthesis of organoelement derivatives of astatine presented above, as the starting compound –

* The constancy of the specific activities apparently indicates not only the isomorphism of the compounds $PhJCl_2$ and $PhAtCl_2$, but also the closeness of the crystallization coefficient for the system $PhJCl_2$–$PhAtCl_2$–chloroform to unity.

for obtaining $PhJ(At)O_2$, $PhJ(At)Cl_2$ can also be used.

The synthesis was carried out as follows. Crystals of $PhJ(At)Cl_2$ were placed in a centrifuge tube, to which 2 ml of a 50% NaOH solution and 0.5 ml of acetic acid were added. The mixture was heated to boiling and chlorinated until the crystals of $PhJ(At)Cl_2$ had completely dissolved.* The crystals of $PhJ(At)O_2$ that precipitated upon cooling of the solution were recrystallized from a very small amount of water. The aqueous solution was applied to chromatographic paper. A typical chromatogram is shown in Fig. 4. The position of the α-active peak coincides with the position of the $PhJO_2$ peak.

Fig. 4. Chromatographic behavior of $PhJ(At)O_2$ upon development in acetone. 1 –Ph_2AtCl, 2 –Ph_2JCl

Thus, by the method of classical synthesis the following organoelement deriva-

tives of polyvalent astatine have been obtained: $PhAtCl_2$—astatobenzene chloride, Ph_2AtCl—diphenylastatonium chloride, $PhAtO_2$—astatoxybenzene. The existence of PhAt (astatobenzene) as an intermediate product in the synthesis of the listed compounds has been shown.

Table 1

Main classes of organic derivatives of polyvalent iodine

	Iodihalides	Iodoso compounds	Iodonium compounds	Iodoxy compounds	Iodoxy compounds
General formula	$R-J\begin{matrix}X\\X\end{matrix}$	$ArJ \rightarrow O$	$Ar \cdot J = O$	$[Ar_2J]^+$	$ArJ\begin{matrix}O\\O\end{matrix}$
Valent. group	(2), 2, 6	4, 4	(2), 2, 6	4, 4	2, 6
Absol. valent.	3	3	3	3	5

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* With sufficiently large amounts of $PhJ(At)Cl_2$, the $PhJ(At)O_2$ that forms may be in the precipitate. In this case boiling is continued until the yellow crystalline precipitate of $PhJ(At)Cl_2$ has completely changed into the white amorphous precipitate of $PhJ(At)O_2$.

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