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O. A. Reutov and G. M. Ostapchuk

THE ISOTOPIC-EXCHANGE REACTION OF SYMMETRICAL ORGANOMERCURY COMPOUNDS OF THE AROMATIC SERIES WITH METALLIC MERCURY LABELED WITH Hg203

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In connection with studies of the mechanism of substitution reactions at a carbon atom, using organomercury compounds as examples ($^{1-4}$), we undertook a systematic study of the reactivity of various types of organomercury compounds in isotopic-exchange reactions with metallic mercury and mercuric halide (^{5}).

In the present communication we set forth some results of the study of the isotopic-exchange reaction between diarylmercury and metallic mercury labeled with the radioactive isotope Hg203.

A well-known method for the synthesis of organometallic compounds is the interaction of organomercury compounds with metals (Li, Na, Be, Mg, Zn, Cd, Al, In, Sn, Sb, Bi):

$$\frac{n}{2}R_2Hg + Me \to \frac{n}{2}Hg + R_{nMe} \quad (n \text{ is the valence of the metal } Me).$$

For the most active metals the reaction proceeds at room temperature, but in the case of heavy metals heating to 120–130° is necessary. The mechanism of the reaction has not been studied.

The simplest conceivable model of this reaction is an isotopic-exchange reaction:

$$R_2Hg + \overset{*}{H}g \rightleftarrows R_2\overset{*}{H}g + Hg.$$

We found that symmetrical organomercury compounds of the aromatic series unexpectedly react with metallic mercury under very mild conditions. The rate of the isotopic-exchange reaction

$$X -- Hg -- X + \overset{*}{H}g \rightleftarrows X -- \overset{*}{H}g -- X + Hg$$

depends substantially on the nature of *X*.

The reactions were carried out in organic solvents with vigorous standard stirring (1500 ± 200 rpm) in a thermostated system. To determine the percentage of exchange, diarylmercury was isolated from the reaction mixture as follows: water was added to the dioxane or pyridine solution that had been filtered off from metallic mercury; the precipitated diarylmercury was crystallized from a suitable solvent until a constant melting point and constant radioactivity were attained. If benzene or xylene was used as the solvent, the diarylmercury was precipitated with petroleum ether. To measure radioactivity, the preparations were applied (by dropping the solutions) onto filters 20 mm in diameter, coated with a lacquer of organic glass (1 g of Plexiglas per 100 ml of dichloroethane), and dried.

Measurements of the radioactivity of diarylmercury were carried out on a B-2 apparatus using MST-17 end-window counters and MS-4 γ-counters.

The following figures may give an idea of the rate of isotopic exchange in the reaction under consideration.

For diphenylmercury. In xylene at 140° (diphenylmercury concentration 0.43 mol/l, mercury 3.4 mol/l), equilibrium is established in 30 min.

In dioxane at 60° (diphenylmercury concentration 0.11 mol/l, mercury 1.7 mol/l), equilibrium is established in 2 h 45 min.

For di-*p*-anisylmercury. In dioxane at 60° (dianisylmercury concentration 0.088 mol/l, mercury 1.74 mol/l), equilibrium is reached in 1 h.

In benzene at 20° (dianisylmercury concentration 0.05 mol/l, mercury 0.87 mol/l), equilibrium is established in 16 h.

Exchange is accelerated when the temperature is raised and, up to a certain limit, when the excess of metallic mercury is increased. No effect of the nature of the solvent on the reaction rate was observed.

We subsequently decided to study the dependence of the rate of isotopic exchange on the nature of the substituent X. For this purpose a series of experiments was carried out in pyridine under identical conditions*. The results of these experiments are given in Table 1; from them it follows that the rate of the reaction under consideration

Table 1

Results of isotopic exchange of organomercury compounds with mercury in pyridine

Formula of the organomercury compound	Experiment No.	0.25 h	0.5 h	0.75 h	1 h	1.5 h	2 h	3 h	4 h	5 h	6 h	6.5 h	7 h	7.5 h	8 h	9 h	10 h	14 h	16 h	25 h
$(CH_3O-C_6H_4)_2Hg$	1	9	14	26	46	78	86	86	—	—	—	88								
$(CH_3O-C_6H_4)_2Hg$	2	11	25	41	54	75	89	100												
$(CH_3-C_6H_4)_2Hg$	1	—	—	—	21	37	51	—	79	—	83									
$(CH_3-C_6H_4)_2Hg$	2	—	—	—	18	37	62	82	88	—	92									
$(C_6H_5)_2Hg$	1	—	—	—	3	—	—	22	—	—	80	—	—	—	—	100				
$(C_6H_5)_2Hg$	2	—	—	—	3	—	—	—	—	—	82									
$(C_6H_5)_2Hg$	3	—	—	—	3	—	11	26	58	—	83	—	82							
$(Cl-C_6H_4)_2Hg$	1	—	—	—	—	—	7	—	16	—	28	—	—	—	48	—	62	83	90	98
$(Cl-C_6H_4)_2Hg$	2	—	—	—	—	—	7	—	19	—	40	—	—	—	—	58	—	—	85	93
$(Cl-C_6H_4)_2Hg$	3	—	—	—	—	—	11	—	28	—	48	—	—	—	62	—	74	90	92	96
$(O_2N-C_6H_4)_2Hg$	1	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	69	77	80	
$(O_2N-C_6H_4)_2Hg$	2	—	—	—	0	—	4	—	11	—	—	—	—	—	—	—	—	—	—	98

Notes. 1. The reaction was carried out in pyridine at 60°; the concentration of the organomercury compound was 0.028 mol/l; mercury was taken in a 50-fold gram-equivalent excess. The exception is experiment No. 1 with di-*p*-nitrophenylmercury, where the concentration of the organomercury compound was 0.026 mol/l, and mercury was taken in a 100-fold excess.

2. In all cases the table gives the percentage of exchange relative to equilibrium.

of isotopic exchange, depending on the nature of the substituent X, increases in the sequence:

$$O_2N,\ Cl < H < CH_3 < OCH_3.$$

The accuracy of our experiments** does not allow us to establish which of the organomercury compounds—dinitrophenylmercury or dichlorophenylmercury—reacts faster with metallic mercury.

* All experiments were carried out in the same 250-ml flask equipped with a Witt stirrer at 1500 ± 200 rpm.

** In Table 1, for each organomercury compound the results of two to three parallel experiments are presented. Comparison of them shows that in most cases reproducibility with deviations averaging ~10% is observed.

It is noteworthy that isotope exchange proceeds under very mild conditions, especially in the case of dianisylmercury, which reacts rapidly with metallic mercury even in the cold*.

Under such mild conditions it is hardly possible for the reaction to proceed through the stage of decomposition of diarylmercury and formation of free radicals:

$$(XC_6H_4)_2Hg \rightleftarrows 2XC_6H_4\cdot + \cdot Hg\cdot,$$

$$2XC_6H_4\cdot + {}^*Hg\cdot \rightleftarrows (XC_6H_4)_2{}^*Hg.$$

Apparently, the reaction occurs directly between the molecules of diarylmercury and metallic mercury.

The results of isotope exchange of phenyl-*p*-nitrophenylmercury also testify in favor of this:

$$C_6H_5{-}Hg{-}C_6H_4NO_2 + {}^*Hg \rightleftarrows C_6H_5{-}{}^*Hg{-}C_6H_4NO_2 + Hg.$$

After isotope equilibrium had been reached, only the initial phenyl-*p*-nitrophenylmercury was detected in the reaction mixture. If the reaction proceeded through the stage of formation of free phenyl and nitrophenyl radicals, then in the reaction mixture, after establishment of isotope equilibrium, along with $C_6H_5{-}Hg{-}C_6H_4NO_2$, there should also have been present $(C_6H_5)_2Hg$ and $(O_2NC_6H_4)_2Hg$.

Moscow State University
named after M. V. Lomonosov

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* In contrast to organomercury compounds, the isotope-exchange reaction of organoantimony compounds, as we have shown, proceeds at an appreciable rate only at temperatures above 160°:

$$Ar_3Sb + Sb^{124} \rightleftarrows Ar_3Sb^{124} + Sb.$$

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

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