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Abstract

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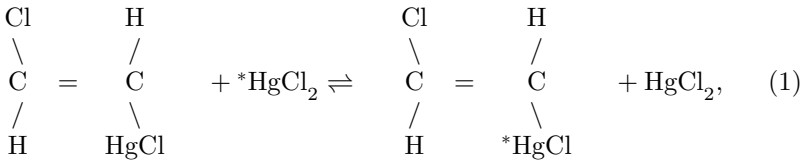
STUDY OF THE STEREOCHEMISTRY OF SUBSTITUTION REACTIONS AT AN OLEFINIC CARBON ATOM BY MEANS OF THE ISOTOPIC METHOD

One of us and A. E. Borisov ([1]), studying metal exchange in a series of stereoisomeric organometallic compounds of the type

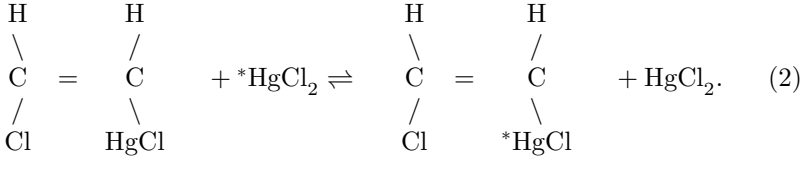
established the following rule: electrophilic and homolytic exchange reactions at an olefinic carbon proceed with retention of the cis- and trans-configuration.

In the present work, by applying the isotopic method, we obtained direct proof of the validity of the rule indicated.

As examples of electrophilic reactions we studied the interaction of trans- and cis-β-chlorovinylmercury chlorides with mercuric chloride labeled with radioactive mercury Hg^{203}. The reactions were carried out in acetone solution in the cold. In both cases we observed the rapid (in less than 5 min) establishment of isotopic equilibrium and, at the same time, strict retention of the initial stereochemical configuration of the chlorovinyl group:



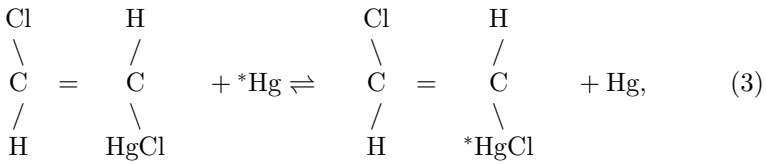
(1)



(2)

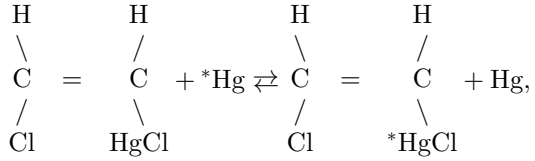
As examples of homolytic reactions we studied the interaction of metallic mercury labeled with Hg^{203} with trans- and cis-β-chlorovinylmercury chlorides, as well as with bis-trans- and bis-cis-β-chlorovinylmercury.*

All four organomercury compounds readily react in acetone in the cold with finely divided metallic mercury. Isotopic equilibrium is established within several hours. All these reactions proceed with complete retention of the stereochemical configuration of the chlorovinyl group:

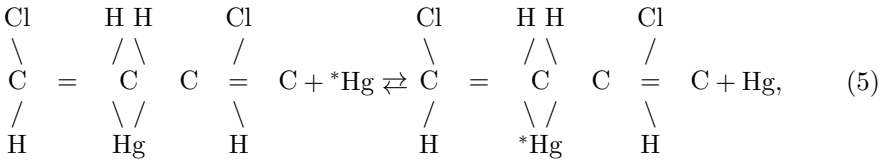


(3)

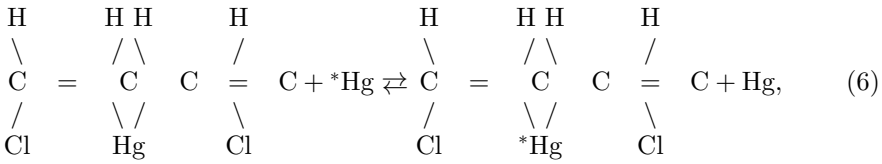
* The possibility of isotopic-exchange reactions of metallic mercury with symmetrical organomercury compounds and with organomercury salts of the aromatic and aliphatic series had been established by us earlier ([2]).



(4)



(5)



(6)

In the interaction of metallic mercury with trans- and cis-β-chlorovinylmercuric chlorides, alongside the isotope-exchange reaction there also occurs a side reaction with the formation of calomel and acetylene:

$$\mathrm{Cl{-}CH{=}CH{-}HgCl} + \mathrm{Hg} \rightarrow \mathrm{H{-}C{\equiv}C{-}H} + \mathrm{Hg_2Cl_2^*}. \qquad (7)$$

Thus, here we have a typical example of dual reactivity, so characteristic of all β-chlorovinyl organometallic compounds.

If the results of isotope exchange of bis-trans- and bis-cis-β-chlorovinylmercury with metallic mercury (reactions (5) and (6)) are direct proof of the preservation of stereochemical configuration in these reactions, then the results of reactions (1)–(4) require additional discussion.

I. P. Beletskaya, R. E. Mardaleishvili, and one of us ([3]), in studying the kinetics of symmetrization of α-bromomercuriphenylacetic acid esters by ammonia, showed that this reaction proceeds in two stages**:

$$\text{(a)} \quad 2\text{R—HgX} \rightleftarrows \text{R}_2\text{Hg} + \text{HgX}_2,$$
$$\text{(b)} \quad \text{HgX}_2 + 2\text{NH}_3 \rightleftarrows \text{HgX}_2 \cdot (\text{NH}_3).$$

If, in the reactions studied by us (1)–(4), an equilibrium of this kind

$$2\text{ClCH=CH—HgCl} \rightleftarrows (\text{ClCH=CH})_2\text{Hg} + \text{HgCl}_2 \tag{8}$$

plays any appreciable role, then both bis-β-chlorovinylmercury and sublimate will enter into isotope exchange with *Hg and $^*\text{HgCl}_2$, respectively. The stereochemistry of reactions (1)–(4) observed by us would then be the result not of one but of several processes. We established, however, by special experiments, that bis-β-chlorovinylmercury is absent from the reaction mixture even in the case of reactions (3) and (4), i.e., when an excess of metallic mercury, which readily converts sublimate into calomel, should have promoted a shift of equilibrium (8) to the right with the formation of noticeable amounts of the symmetrical organomercury compound.

Thus, it may be asserted that reactions (1)–(4) do not proceed through equilibrium, but that HgCl_2^* and *Hg react directly with β-chlorovinylmercuric chlorides. In this connection, the results obtained by us are a direct confirmation of the preservation of configuration at the olefinic carbon atom in electrophilic and homolytic substitution reactions.

* Special experiments showed that calomel labeled with Hg^{203}, under our conditions, does not enter into isotope exchange with β-chlorovinylmercuric chlorides.
** Studying the symmetrization of organomercury salts under the action of KI, Whitmore ([4]) concluded that this reaction also proceeds through equilibrium.

Experimental Part

1. Interaction of trans-β-chlorovinylmercury chloride with sulema labeled with Hg^{203}. In a 25-ml volumetric flask, 0.1488 g (0.0005 mole) of trans-β-chlorovinylmercury chloride, m.p. 122°, and 0.1359 g (0.0005 mole) of sulema labeled with Hg^{203} were dissolved in acetone at 23°. The solution was transferred to an evaporating dish and evaporated to dryness in the cold under

a stream of air. To separate the chlorovinylmercury chloride from the sulema, the precipitate was dissolved in 50 ml of ether, and the sulema was extracted from the ether with five portions (50 ml each) of a saturated aqueous solution of sodium chloride. The ethereal solution of chlorovinylmercury chloride was evaporated in the cold; the precipitate was dried in a desiccator over a mixture of calcium chloride and caustic soda*. After recrystallization from acetone, trans-β-chlorovinylmercury chloride has m.p. 120°. A mixed melting test with authentic trans-β-chlorovinylmercury chloride: 121°. Before the radioactivity measurement, trans-β-chlorovinylmercury chloride was recrystallized twice from acetone. Isotopic exchange proceeded to 99%**.

2. Interaction of cis-β-chlorovinylmercury chloride with sulema labeled with Hg^{203}. In a 25-ml volumetric flask, 0.1484 g (0.0005 mole) of cis-β-chlorovinylmercury chloride, m.p. 78°, and 0.1355 g (0.0005 mole) of sulema labeled with Hg^{203} were dissolved in acetone at 23°. The solution was transferred to an evaporating dish and evaporated to dryness in the cold under a stream of air. The solid residue was extracted (twice, 20 ml each time) with carbon tetrachloride. The solution of cis-β-chlorovinylmercury chloride was filtered off and evaporated to dryness. The cis-β-chlorovinylmercury chloride was recrystallized from acetone. M.p. 79°. A mixed melting test with authentic cis-β-chlorovinylmercury chloride: 78° (with authentic trans-β-chlorovinylmercury chloride: 92°)***. Isotopic exchange proceeded to 92%.

3. Interaction of trans-β-chlorovinylmercury chloride with metallic mercury labeled with Hg^{203}. In a 200-ml flask equipped with a reflux condenser, a pipette for taking samples, and a Witt stirrer (3000 $\pm$ 200 rpm), a solution of trans-β-chlorovinylmercury chloride in acetone (concentration 0.05 mole/liter) and metallic mercury (40-fold gram-equivalent excess) were stirred. Several minutes after the start of stirring, formation of calomel and acetylene was observed. Samples for determination of radioactivity were taken at specified intervals, in such a calculation that the total amount of solution withdrawn as samples did not exceed 10% of that taken for the reaction.

a. Carrying out the reaction at 23°:

Exchange time, hr	0.58	1.33	2.33	4.42	6.17
Percent exchange	7	24	31	53	64

M.p. of the starting substance 122°. M.p. of trans-β-chlorovinylmercury chloride isolated from the reaction mixture, 119°. A mixed melting test with authentic trans-β-chlorovinylmercury chloride: 120°.

* Separation of a mixture of chlorovinylmercury chloride and sulema can also be carried out with the aid of carbon tetrachloride, in which the organomercury compound dissolves, while sulema is practically insoluble.

** Measurement of the radioactivity of preparations containing Hg^{203} was carried out on a B-2 apparatus with end-window MST-17 counters. The preparations were deposited (by dropwise application of solutions) on filters 20 mm in diameter, coated with organic-glass varnish (5 g of plexiglass in 200 ml of dichloroethane), and dried. The preparations, wrapped in tracing paper, were placed at the center between the windows of two MST-17 counters, mounted on a stand in a lead housing IFKh-2 and connected in parallel to the cathode follower of a BGS. In all cases the experimental error was 5–10%.

*** The dependence curve of the melting temperature of mixtures of cis- and trans-β-chlorovinylmercury chlorides on their composition has no minimum (linear dependence).

b. Carrying out the reaction at 35°

Exchange time, h	1.00	1.33	1.66	2.00	2.50	3.75
Percent exchange	39	60	65	82	98	97

M.p. of the starting substance 122°. M.p. after the reaction 119°. A mixed melting-point sample with authentic trans-β-chlorovinylmercury chloride: 120°.

4. **Interaction of cis-β-chlorovinylmercury chloride with metallic mercury labeled with Hg^{203}.** When the reaction of cis-β-chlorovinylmercury chloride with metallic mercury labeled with Hg^{203} was carried out under the conditions of the preceding experiment, the following results were obtained.

a. Carrying out the reaction at 23°:

Exchange time, h	0.42	1.08	2.00	3.50	4.50
Percent exchange	8	18	26	36	74

The initial cis-β-chlorovinylmercury chloride melts at 79°; after the reaction, at 77°. A mixed sample with authentic cis-β-chlorovinylmercury chloride melts at 78°.

b. Carrying out the reaction at 35°:

Exchange time, h	0.25	0.58	0.92	1.16	1.42
Percent exchange	24	36	54	55	65

The starting substance melts at 79°; after the reaction, at 76°. A mixed sample with authentic cis-β-chlorovinylmercury chloride melts at 77°.

5. **Interaction of bis-trans-β-chlorovinylmercury with metallic mercury labeled with Hg^{203}.** The reaction of bis-trans-β-chlorovinylmercury (0.05 M acetone solution) with metallic mercury (40-fold gram-equivalent excess) labeled with Hg^{203} was carried out under the conditions of experiments 3 and 4.

a. Carrying out the reaction at 23°:

Exchange time, h	2.25	6.58	7.83	10.50
Percent exchange	20	48	61	71

M.p. of the starting substance: 62°. M.p. after the reaction: 61°.

b. Carrying out the reaction at 35°:

Exchange time, h	1.25	2.25	3.66	5.25	6.25	9.25
Percent exchange	55	65	85	96	90	100

M.p. of the starting substance 64°. M.p. after the reaction 63°.

6. **Interaction of bis-cis-β-chlorovinylmercury with metallic mercury labeled with Hg^{203}.** Under the conditions of the preceding experiment, the reaction at 23° of bis-cis-β-chlorovinylmercury (liquid) with metallic mercury labeled with Hg^{203} was carried out. After 8 h the exchange reaches 90%. Both before and after the reaction, bis-cis-β-chlorovinylmercury, upon interaction with sublimate, gives pure cis-β-chlorovinylmercury chloride.

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