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Abstract

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On the Stereochemistry of Isotopic-Exchange Reactions of Organomercury Salts with Metallic and Halide Mercury Labeled with Hg^{203}

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In the course of studying the mechanism of isotopic exchange of organomercury compounds with metallic and halide mercury $^{(1-4)}$, it became necessary to determine the stereochemistry of the following reactions:

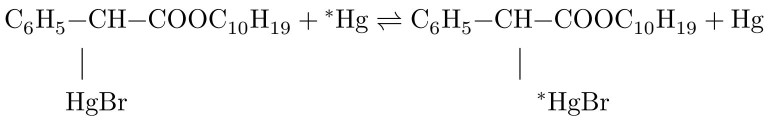
$$R_1R_2R_3C{-}HgX + {}^*Hg \rightleftharpoons R_1R_2R_3C{-}{}^*HgX + Hg \qquad (1)$$

$$R_1R_2R_3C{-}HgX + {}^*HgX_2 \rightleftharpoons R_1R_2R_3C{-}{}^*HgX + HgX_2 \qquad (2)$$

Reaction (1) is a process of homolytic substitution, whereas reaction (2) is one of electrophilic substitution at a saturated carbon atom.

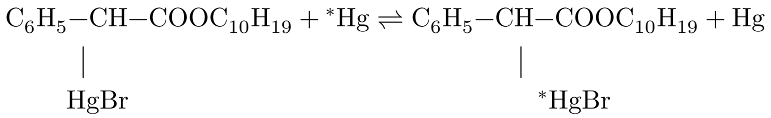
In the present article we describe the results of a study of the stereochemistry of reaction (1) using as an example the diastereomeric *l*-menthyl esters of α-bromomercuriphenylacetic acid, and of reaction (2) using as an example the cis- and trans-isomers of 2-methoxycyclohexylmercuric chloride.

Both diastereomers of the *l*-menthyl ester of α-bromomercuriphenylacetic acid —(I), with $[\alpha]_D^{18} - 86° \pm 2$, and (II), with $[\alpha]_D^{18} - 49° \pm 2$—readily react with finely divided metallic mercury in the cold in anhydrous benzene. In both cases complete retention of the stereochemical configuration at the α-carbon atom was established: the angles of rotation of the diastereomers before the reaction and after establishment of isotopic equilibrium proved to be identical.



$$\underset{\displaystyle HgBr}{C_6H_5{-}\underset{|}{C}H{-}COOC_{10}H_{19}} + {}^*Hg \rightleftharpoons \underset{\displaystyle {}^*HgBr}{C_6H_5{-}\underset{|}{C}H{-}COOC_{10}H_{19}} + Hg$$

$$(I) \quad [\alpha]_D^{18} - 86° \pm 2 \qquad\qquad [\alpha]_D^{18} - 85.7° \pm 2$$



$$C_6H_5-\underset{\displaystyle HgBr}{\underset{|}{CH}}-COOC_{10}H_{19} + {}^*Hg \rightleftharpoons C_6H_5-\underset{\displaystyle {}^*HgBr}{\underset{|}{CH}}-COOC_{10}H_{19} + Hg$$

$$\text{(II)} \quad [\alpha]_D^{18} - 52^\circ \pm 2 \qquad\qquad [\alpha]_D^{18} - 49.6^\circ \pm 2$$

Retention of the stereochemical configuration of the saturated carbon atom in reactions of isotopic exchange of organomercury salts with radioactive metallic mercury is further evidence that these homolytic reactions are not free-radical reactions, since in the case of intermediate formation of free radicals $R_1R_2R_3C\cdot$, the stereochemical result of these reactions would be racemization.

Molecules of organomercury compounds apparently react directly with mercury molecules*:

$$R_1R_2R_3C-Hg-X+{}^*Hg \rightleftharpoons \left[\begin{array}{c} R_1R_2R_3C\cdots Hg\cdots X \\ \ddots \quad {}^*Hg \quad \ddots \end{array}\right] \rightleftharpoons R_1R_2R_3C-{}^*Hg-X+Hg$$

To elucidate the stereochemistry of the isotopic-exchange reaction with halogen mercury, the diastereomeric *l*-menthyl esters of α-bromomercuriphenylacetic acid proved unsuitable, since mercuric bromide causes rapid "racemization" of both diastereomers (at the α-carbon atom), even under such mild conditions that isotopic exchange does not occur at all.

In this connection, cis- and trans-2-methoxycyclohexylmercury chlorides were chosen as objects for studying the reaction with halogen mercury. The melting points of the cis- (114°) and trans-isomer (115°) differ very little from one another; however, the mixed melting point (~ 85°) of the cis- and trans-isomers shows a large depression. This circumstance greatly facilitates identification of both isomers.

The isotopic-exchange reaction was carried out in dioxane, acetone, and isobutyl alcohol. Isotopic exchange proceeds at an appreciable rate only at temperatures of 120–135°**.

In all cases, strict retention of the initial stereochemical configuration of the substances was established:

$$\text{cis-2-methoxycyclohexylmercury chloride} + {}^*HgCl_2 \rightleftharpoons \text{cis-2-methoxycyclohexyl-}{}^*\text{mercury chloride} + HgCl_2$$

$$\text{trans-2-methoxycyclohexylmercury chloride} + {}^*HgCl_2 \rightleftharpoons \text{trans-2-methoxycyclohexyl-}{}^*\text{mercury chloride} + HgC$$

Thus, the isotopic-exchange reaction under consideration, being a process of electrophilic substitution at a saturated carbon atom, proceeds with retention of configuration. It should be noted that this same result has also been observed for all other studied reactions of electrophilic substitution at a saturated carbon atom, except for the cases reported by Cram (^{5}).

Experimental Part

Interaction of diastereomer (I) ($[\alpha]_D^{18} - 86^\circ$) of the *l*-menthyl ester of α-bromomercuriphenylacetic acid with metallic mercury labeled with Hg^{203}. A solution of 0.50 g ($9 \cdot 10^{-4}$ mole) of the diastereomeric *l*-menthyl ester of α-bromomercuriphenylacetic acid with $[\alpha]_D^{18} - 86^\circ$ and m.p. 153° in 60 ml of abs. benzene (concentration 0.015 mole/liter) and 20 g of metallic mercury (111-fold gram-equivalent excess) labeled with Hg^{203} is vigorously stirred (Witt stirrer at 2500 ± 200 rpm) in the cold for 15 hours. After completion of the reaction, the metallic mercury is filtered off. To free the solution of the substance from colloidal mercury, it is passed through a chromatographic column with alumina. After this the solution is evap—

* Alternative mechanism

$$R_1R_2R_3C{-}HgX + {}^*Hg \rightleftharpoons R_1R_2R_3C{-}Hg{-}{}^*Hg{-}X \rightleftharpoons R_1R_2R_3C{-}{}^*Hg{-}X + Hg$$

seems to us less probable.

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Under these conditions, along with exchange, decomposition of the starting substances with formation of calomel occurs in appreciable amounts.

are filtered in the cold under a stream of dry air. The dry residue, weighing 0.46 g, is dissolved with heating in a minimal amount of carbon tetrachloride; several drops of methyl alcohol are added to the solution, and it is cooled to −10°. On rubbing the walls of the vessel with a glass rod, the substance crystallizes. Weight 0.35 g (70% of theory). M.p. 153-154°; $[\alpha]_D^{18} = 85.7^\circ \pm 2$ ($C = 0.854$; $l = 1.9$; $\alpha = -0.95^\circ \pm 0.02$)*.

Measurement of the radioactivity of the preparation shows that exchange has proceeded to 100%, i.e., the activity of the preparation is equal to the equilibrium activity.

Parallel experiments on the interaction of diastereomer (I) with radioactive metallic mercury give well-agreeing results.

Interaction of diastereomer (II) ($[\alpha]_D^{18} - 52^\circ$) **of the l-menthyl ester of α-bromomercuriphenylacetic acid with metallic mercury labeled with Hg^{203}.** A solution of 0.35 g ($6.3 \cdot 10^{-4}$ mol) of the diastereomer of the l-menthyl ester of α-bromomercuriphenylacetic acid with $[\alpha]_D^{18} -52°$ and m.p. 144–146° in 42 ml of abs. benzene (concentration 0.015 mol/l) and 20 g of metallic mercury (159-fold g-equivalent excess) labeled with Hg^{203} is vigorously stirred in the cold for 15 h. The mercury is filtered off, the filtrate is passed through a column of alumina, after which the solvent is evaporated in the cold. The dry residue weighs 0.32 g. After recrystallization from carbon tetrachloride, carried out as in the preceding experiment, the weight of the substance is 0.24 g (68% of theory). M.p. 145–146°; $[\alpha]_D^{18} - 49.6° \pm 2°$ ($C = 0.584$; $l = 1.9$; $\alpha = -0.55° \pm 0.02°$). Measurement of the radioactivity of the preparation shows that exchange has proceeded to 100%.

Interaction of trans-2-methoxycyclohexylmercuric chloride with mercuric chloride labeled with Hg^{203}. A solution containing equimolecular amounts of trans-2-methoxycyclohexylmercuric chloride and mercuric chloride labeled with Hg^{203} is kept for a definite time at constant temperature in a sealed ampoule or in a test tube equipped with a reflux condenser. After the reaction is complete, the solvent is evaporated in the cold, and trans-2-methoxycyclohexylmercuric chloride is extracted from the precipitate with cold carbon tetrachloride. Before measurement of radioactivity and determination of the melting point, the substance is crystallized twice from methyl alcohol. The results of the experiments carried out by us are summarized in Table 1.

Table 1[1]

Experiment no.	Molar concentration of reacting substances	Reaction temp., °C	Solvent	Exchange time, h	Activity of preparation, imp/min · mg Hg	Equilibrium activity, imp/min · mg Hg	Percent exchange
1	0.05	23	Acetone	25	5	1140	0
2	0.05	50	Acetone	6	95	2520	4
3	0.1	98	Acetone	0.5	30	486	6
4	0.1	98	Acetone	1.0	32	486	7
5	0.1	98	Acetone	2.0	6	486	1
6	0.1	135	Acetone	0.5	77	1400	6
7	0.1	135	Acetone	1.5	178	1400	13
8	0.1	135	Acetone	3.0	284	1400	20
9	0.1	120	Dioxane	9.5	1250	1900	66
10	0.1	130	Dioxane	3.0	1095	1900	58

[1] Experiments nos. 3–10 were carried out in sealed ampoules.

Determination of the melting points of the 2-methoxycyclohexylmercuric chloride isolated after the reaction and of its mixtures with known trans- and cis-isomers gave the following identical results in all experiments: the substance, isolated after the reaction melted at 113°, i.e., in the same way as before the reaction; a mixed sample of the substance with the cis isomer melted at 84-86°; a mixed sample with the known trans isomer melted at 112-113°.

Interaction of cis-2-methoxycyclohexylmercury chloride with sublimate labeled with Hg^{203}. The isotopic-exchange reaction and isolation of the substance were carried out in the same way as in the case of the trans isomer. The results of the experiments are summarized in Table 2.

Table 2

Experiment no.	Molar concentration of reacting substances	Reaction temp., °C	Solvent	Exchange time, h	Activity of preparation, imp/min· mg Hg	Equilibrium activity, imp/min· mg Hg	Percent exchange
1	0.01	80	Isobutyl alcohol	4	18	2360	1
2	0.05	80	Same	8	24	486	5
3	0.05	80	”	16	28	486	6
4	0.1	120	Dioxane	9.5	147	1900	8
5	0.1	130	”	10	1205	1900	63

Determination of the melting points of the 2-methoxycyclohexylmercury chloride isolated after the reaction and of its mixtures with known cis and trans isomers gave the following identical results in all experiments: the substance isolated from the reaction mixture melted at 112°; a mixed sample with the known cis isomer melted at 112-113°; a mixed sample with the known trans isomer melted at 84-85°.

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* Special experiments showed that a known mixture of diastereomers consisting of 70% (I) and 30% (II) cannot be separated with isolation of pure (I) as a result of the treatment used by us in the experiment.

CITED LITERATURE

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