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Abstract

Full Text

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Interaction of Diisopropylmercury with Chloroform and Carbon Tetrachloride

Previously we showed ([1]) that readily oxidized alkyl mercury compounds, such as, for example, diisopropyl- and dicyclohexylmercury, react with $CHCl_3$ and CCl_4 under the action of atmospheric oxygen. The main product of the interaction is alkylmercury chloride. At the same time it was proved that a process of oxidation of the radicals bonded to mercury also takes place, with formation of the corresponding alcohols and ketones. The reaction initiated by oxygen is a complex chain process. Therefore it seemed advisable to us to study a simpler reaction of dialkylmercury with $CHCl_3$ and CCl_4, carrying it out in the absence of oxygen and at the temperature at which the above organomercury compounds begin to decompose, i.e., about 130°. This was all the more so because earlier work on photo- and thermoreactions of more stable organomercury compounds with the indicated alkyl halides was carried out in an air atmosphere and concerned a more detailed study of aryl derivatives ([2]). Among alkyl derivatives, mercury compounds with primary radicals (methyl ([3]) and ethyl ([4])) had been investigated insufficiently. It was established that the reactions are initiated by free radicals formed from the organomercury compound or the solvent.

Diisopropylmercury (DIPR), containing a secondary alkyl radical, was chosen as the object of the present investigation. To carry out the reaction, chloroform $CDCl_3$ labeled with deuterium (to 99%) was used. The use of heavy chloroform makes it possible to estimate the degree of interaction with it of isopropyl radicals (DIPR) formed from the organomercury compound.

The reactions of DIPR with $CDCl_3$ and CCl_4 were carried out at 130° for 10 h. Their products are isopropylmercury chloride, mercury, propane, propylene, isopropyl chloride, and chloroform. In the case of the first solvent, 2-deuteropropane and monodeuterodichloromethane are also formed, and with CCl_4, hexachloroethane and a small amount of calomel (Table 1).

The presence of isopropyl chloride in considerable amount (31.4%) in the products of the reaction of DIPR with $CDCl_3$ was unexpected for us. It is known ([5]) that both aryl and alkyl radicals formed as a result of dissociation of an organomercury compound abstract from chloroform only hydrogen; abstraction of chlorine was not observed. One might suppose that the formation of isopropyl chloride is due to an isotope effect. Therefore, in order to test this supposition, the reaction of DIPR with ordinary chloroform was carried out (see Table 1).

As is evident from the data in the table, isopropyl chloride is also present, but in a considerably smaller amount than in the first case. Propane, on the other hand, is formed in an amount almost 20% greater than in the reaction with $CDCl_3$ (see table). Thus, the isotope effect does indeed influence the yield of chloropropane. The presence of the latter in large amount (51.4%) in the products of the reaction of DIPR with CCl_4 indicates the possibility of abstraction of chlorine by an alkyl radical from a chlorine-containing solvent.

On the basis of the experimental data, the process of decomposition of DIPR in $CHCl_3$ and CCl_4 may be represented in the following way. Initially, mercury-

Table 1

Reaction product	$CDCl_3$, mol	$CDCl_3$, mol. %	CCl_4, mol	CCl_4, mol. %	$CHCl_3$, mol	$CHCl_3$, mol. %
Reaction of 0.0035 mole of (iso-$C_3H_7)_2$Hg with 0.06 mole of $CDCl_3$ and CCl_4, 130°, 10 h						
Hg	0,0008	22,8	0,0001	2,9	–	–
Hg_2Cl_2	–	–	0,0001	2,9	–	–
iso-C_3H_7HgCl	0,0027	77,1	0,0031	88,6	–	–
C_3H_7D	0,0009	25,7	–	–	–	–
C_3H_8	0,0004	11,4	0,0003	8,6	–	–
C_3H_6	0,0004	11,4	0,0004	11,4	–	–
iso-C_3H_7Cl	0,0011	31,4	0,0018	51,4	–	–
$CHCl_3$	0,0008	22,8	0,0017	48,6	–	–
$CDHCl_2$	0,0007	20	–	–	–	–

Reaction product	$CDCl_3$, mol	$CDCl_3$, mol. %	CCl_4, mol	CCl_4, mol. %	$CHCl_3$, mol	$CHCl_3$, mol. %
Reaction of 0.0031 mole of (iso-$C_3H_7)_2$Hg with 0.053 mole of $CHCl_3$						
Hg	–	–	–	–	0,0007	22,6
iso-C_3H_7HgCl	–	–	–	–	0,0024	77,4
C_3H_8	–	–	–	–	0,0017	54,9
C_3H_6	–	–	–	–	0,0003	9,7
iso-C_3H_7Cl	–	–	–	–	0,0004	12,9
CH_2Cl_2	–	–	–	–	0,0006	19,3

the organometallic compound dissociates into radicals:

$$(\text{iso-}C_3H_7)_2Hg \rightarrow \text{iso-}C_3H_7\cdot + \text{iso-}C_3H_7Hg\cdot \tag{1}$$

The isopropylmercury radical reacts with chloroform or carbon tetrachloride, and also partly decomposes into mercury and an isopropyl radical:

$$\text{iso-}C_3H_7Hg\cdot \begin{cases} \xrightarrow{CCl_4} \text{iso-}C_3H_7HgCl + Cl_3C \\ \xrightarrow{CDCl_3} \text{iso-}C_3H_7HgCl + Cl_2DC \end{cases} \quad \downarrow \quad \text{iso-}C_3H_7\cdot + Hg \tag{2}$$

The isopropyl radicals formed react with DIPR (^{6}), with formation of propane and propylene

$$\begin{gathered} \text{iso-}C_3H_7\cdot + (\text{iso-}C_3H_7)_2Hg \rightarrow C_3H_8 + \text{iso-}C_3H_7Hg\dot{C}(CH_3)_2 \\ \downarrow \\ \text{iso-}C_3H_7Hg\cdot\ C_3H_6 \end{gathered} \tag{3}$$

or with the solvent:

$$\text{iso-}C_3H_7\cdot + CCl_4 \rightarrow \text{iso-}C_3H_7Cl + Cl_3C \tag{4a}$$

$$\text{iso-}C_3H_7\cdot + CDCl_3 \begin{cases} \rightarrow C_3H_7D + Cl_3C \\ \rightarrow \text{iso-}C_3H_7Cl + Cl_2DC \end{cases} \tag{4b}$$

As is seen from the data in the table, the ease of abstraction of hydrogen, deuterium, and chlorine from chloroform is in the following relation: $H > Cl \sim D$, and it is evident that in the reaction of DIPR with $CDCl_3$ about 20% monodeuterodichloromethane, $CDHCl_2$, is formed. Its formation occurs as a result of abstraction of a hydrogen atom from a hydrogen-donor compound by the corresponding radical. DIPR or the hydrocarbons formed may serve as the hydrogen-donor compound. One could also have assumed disproportionation of the $CDCl_2$ radical. However, dideuterodichloromethane, CD_2Cl_2, was not detected in an appreciable amount.

In the course of the reaction of DIPR with $CDCl_3$, the appearance of ordinary chloroform was observed (about 23% relative to the organomercury compound). The formation of po-

the latter occurs in a fairly large amount (48.6%) in the reaction with CCl_4. This indicates that secondary trichloromethyl radicals interact with DIIPR with abstraction of a hydrogen atom, according to an equation analogous to (3), with formation of saturated ([7]) and unsaturated ([8]) hydrocarbons. It could also be assumed that trichloromethyl radicals enter into exchange reactions (radical transfer) with $CHCl_3$ and CCl_4; however, as is known ([9]), these do not proceed. Some of these radicals dimerize to hexachloroethane, which was not quantitatively analyzed:

$$2Cl_3C\cdot \rightarrow CCl_3CCl_3. \tag{5}$$

On the basis of the data in the table, its yield should be about 48% in the reaction of DIIPR with CCl_4, i.e., about 1/3 of all the Cl_3C-radicals formed is converted into chloroform, and 2/3 dimerizes.

It might have been expected that trichloromethyl radicals also add to the propylene being formed or to isopropyl radicals. However, as a result of alkaline hydrolysis of the reaction product, chlorobutyric and isobutyric acids were not isolated in appreciable amounts in the reactions either with $CHCl_3$ or with CCl_4. Consequently, such a process is unlikely for our system.

Calomel is present in the products of the reaction of DIIPR with CCl_4. It could be assumed that its formation is associated with decomposition of isopropylmercury chloride. However, in the reaction with $CHCl_3$, carried out under analogous conditions, calomel is absent, which indicates that this compound is stable under the reaction conditions. It is evidently formed as a result of the interaction of mercury, liberated during partial decomposition, according to equation (2), of isopropylmercury radical, with CCl_4. It is known (^{10}) that such a process occurs:

$$2Hg + 2CCl_4 \rightarrow Hg_2Cl_2 + C_2Cl_6. \qquad (6)$$

In both the reaction of DIIPR with $CHCl_3$ and that with CCl_4, liquid hydrocarbons are also formed, which were not identified.

Thus, the decomposition reactions of DIIPR in carbon tetrachloride and chloroform are analogous in character and mutually complementary. The experimental data presented and the reaction schemes proposed on their basis confirm the previously obtained results (^{1}) on oxygen-initiated interaction of organomercury compounds with the indicated polyhaloalkanes.

Analysis of the reaction products was carried out on an MI-1305 mass spectrometer.

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