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OXIDATION OF DICYCLOHEXYLMERCURY

Organomercury compounds are convenient for the study of free-radical reactions. In previous works we have widely used for this purpose the thermal and photodecomposition of alkyl and aryl mercury derivatives in various solvents.

It seemed interesting to us to investigate the behavior of the cyclohexyl radical, which we intended to obtain during the decomposition of dicyclohexylmercury (DCHM). According to the literature data (^{1}), this compound is obtained by the Grignard reaction and is a white crystalline substance with m.p. 78-79°. It has been noted that it is unstable and readily decomposes in the light during storage. Indeed, the DCHM obtained in air quickly begins to decompose with liberation of mercury. However, when the thermal decomposition of this substance was carried out in sealed tubes under vacuum, it turned out that its decomposition begins only above 130°.

In the course of the work it was found that the stability of DCHM is strongly affected by atmospheric oxygen. In the absence of oxygen it is quite stable and can be stored in diffused light for an indefinitely long time. Recently a number of works have appeared on the oxidation of organometallic compounds. Thus, organic cadmium compounds are readily oxidized (^{2}). As for mercury compounds, as far as we know, their oxidation by air under ordinary conditions has not yet been described in the literature.

We established that the decomposition of DCHM during storage in the presence of atmospheric oxygen at room temperature and in the dark is accompanied by the formation of oxidation products—cyclohexanone and cyclohexanol. Therefore we decided to dwell in more detail on the oxidation of DCHM in various solvents. The reaction proceeds more simply in alcoholic solutions. When a stream of oxygen is passed through a reaction solution of DCHM in isopropyl alcohol at ordinary temperature, liberation of mercury is observed. In the solution, cyclohexanol and cyclohexanone were found as the main products in equal molar amounts: 0.0081 : 0.0081 per 0.019 mole of DCHM. Consequently, the course of the reaction may be represented as follows: DCHM, adding oxygen, forms an unstable peroxide, which then decomposes into cyclohexanone and cyclohexanol:

$$(C_6H_{11})_2Hg \longrightarrow [(C_6H_{11})_2Hg \cdot O_2] \longrightarrow C_6H_{11}OH + C_6H_{10}O + Hg \qquad (1)$$

No cyclohexane or cyclohexene was detected in the reaction products, but acetone was present in the amount of 0.004 mole; its formation can be explained by oxidation of isopropyl alcohol, which occurs in the presence of DCHM. The mercury balance in the fraction taken for distillation was 96.4%, and for C_6H_{11}-radicals, including the residue, 87%.

The reactions proceed more complicatedly in solvents containing chlorine—$CHCl_3$ and CCl_4. The main product in these reactions is cyclohexylmercury chloride, $C_6H_{11}HgCl$. In chloroform it was found in the amount of 0.01 mole per 0.015 mole of DCHM (70%). A rather considerable liberation of mercury was noted—

0.003 mole (20%). Among the other products, 0.01 mole of cyclohexanol (70%), 0.007 mole of cyclohexanone (47%), and a small amount of cyclohexene and cyclohexane—0.0007 mole each (5% each)—were detected. The mercury balance is 90%, and that for C_6H_{11} is 197 mole %. Judging from the separation of mercury, it may be assumed that, according to equation (1), the reaction proceeds only to the extent of 20%, giving 40% cyclohexanol and cyclohexanone. In all, however, the oxidation products amount to 117%. The excess amount of cyclohexanol and cyclohexanone can apparently be explained by the reaction of DCHR with $CHCl_3$, initiated by an intermediate peroxide compound and proceeding with formation of cyclohexylmercuric chloride:

$$(C_6H_{11})_2Hg + CHCl_3 \rightarrow C_6H_{11}HgCl + [C_6H_{11}\cdot + CHCl_2\cdot] \qquad (2)$$

According to literature data (3), it is known that the separation of alkyl- and arylmercuric chlorides from solutions of mercury compounds in CCl_4 is accelerated in the presence of added peroxides. In addition, we observed that the formation of cyclohexylmercuric chloride in this reaction in vacuum occurs only upon heating to 100°.

In our opinion, in reaction (2) the C_6H_{11}-radical does not interact with the solvent, since cyclohexane was not found in appreciable amount. It is, in all probability, a substantial source of oxidation products (77%). On oxidation, it gives a new $C_6H_{11}O$-radical, which reacts by abstracting a hydrogen atom from $CHCl_3$, since the presence of cyclohexanol relative to cyclohexanone was found in a molar ratio of $1.4 : 1$. To a lesser extent, the C_6H_{11}-radical disproportionates (10 mole %).

The reaction in CCl_4 proceeds still more complexly. In the oxidation of DCHR, 20 mole % each of cyclohexanol and cyclohexanone, and 4 mole % each of cyclohexene and cyclohexane, were found. The main product, with a yield of 76%, was cyclohexylmercuric chloride; about 5% mercury was also found. Reaction (1) evidently proceeds only slightly, giving only 10 mole % of cyclohexanol and cyclohexanone. The main process, as in $CHCl_3$, is the interaction of DCHR with CCl_4 according to equation (2), initiated by the peroxide, with formation of cyclohexylmercuric chloride.

However, C_6H_{11}-radicals in CCl_4 solution, along with oxidation products (30%) and disproportionation (8%), give chlorine-containing products from interaction with the solvent (about 50%), which were established only qualitatively. The mercury balance is 81%, and that for C_6H_{11}-radicals, including the chlorine-containing products, is about 174 mole %.

The presence of free radicals in the reactions of DCHR is confirmed by the rapid disappearance of the violet color of an alcoholic solution of diphenylpicrylhydrazyl. Initiation of polymerization processes is another proof of the formation of free radicals. We tested DCHR as an initiator of polymerization of various monomers: acrylonitrile, methyl methacrylate, methyl acrylate, acrylic acid, and vinyl chloride. The use of organometallic compounds as polymerization initiators (apart from the Ziegler and Natta systems) was investigated by Koton (4). He found that organic mercury compounds initiate polymerization, but very weakly and at elevated temperature.

In our case, under ordinary conditions the reaction likewise did not proceed; however, when oxygen was removed from the system, polymerization occurred at room temperature. Thus, methyl methacrylate with the addition of 0.5 and 1% DCHR polymerized in 5 h by 5-6% at 30°. At 50°, this monomer with the addition of 1.25% DCHR was converted completely into a solid polymer in 28 h. Polymerization of acrylonitrile, methyl acrylate, and acrylic acid proceeds with a higher degree of conversion.

It may be assumed that under conditions in which oxygen is present, the oxidation reaction of DCHR occurs. The peroxide compound formed in this process decomposes without initiating polymerization.

As already indicated above, we investigated the oxidation of DChM in isopropyl alcohol, chloroform, and carbon tetrachloride. The reaction product was analyzed on an IKS-14 in the absorption region 400-2000 cm^{-1}. For quantitative determination of the components, a calibration curve was constructed from standards prepared in the corresponding solvents, in the coordinates: optical density (D)—concentration (C, %).

Oxidation of DChM in isopropyl alcohol. A solution of 6.9 g (0.019 mole) of DChM in 45 ml (0.7 mole) of isopropyl alcohol was oxidized for 40 h with gentle bubbling of dry oxygen (0.3 l/h) through the reaction solution. To accelerate the reaction, the solution was thermostated at 60°. Mercury soon began to precipitate. The amount of mercury liberated was 2.43 g (64.4% of the initial amount). In the filtrate (34.5 g), unreacted DChM was detected. 22.1 g of the filtrate was distilled. The following fractions were obtained: 1) b.p. 81-130°, main 81-83° (18.4 g); 2) b.p. 130-155°, main 150-155° (1.84 g), and 3) a residue containing 0.4 g of a yellow viscous oil and 0.77 g of mercury, corresponding to 32% of the DChM decomposed during distillation.

Acetone was found in the first fraction; it was identified in the form of the corresponding 2,4-dinitrophenylhydrazone, m.p. 125° (from ethanol); a mixed-melting test gave no depression. The amount of acetone was determined by titration of hydrochloric hydroxylamine; 0.004 mole was found per 0.019 mole of the initial DChM. Cyclohexene and cyclohexane were not detected.

In the second fraction only three products were found: cyclohexanol, 0.81 g (44%); cyclohexanone, 0.79 g (43%); and isopropyl alcohol. For quantitative analysis of cyclohexanone, the characteristic absorption band of the stretching vibration of the C=O group at a frequency of 1700 cm^{-1} was used; for cyclohexanol, the absorption band of the vibration of the C–OH group at a frequency of 1060 cm^{-1} was used, and the absorption band of the C–OH group of isopropyl alcohol did not interfere with the determination of cyclohexanol, since it proved to be shifted toward higher frequencies.

The still residue was not identified by individual components; however, the presence of cyclohexanol and cyclohexanone was established.

Oxidation of DChM in $CHCl_3$. 5.5 g (0.015 mole) of DChM in 29 g (0.25 mole) of $CHCl_3$ was oxidized at 25° for 25 h by the method described above. 0.6 g of mercury was isolated (20% of the initial amount). The filtrate (29 g) was analyzed directly for its content of cyclohexanol and cyclohexanone. For quantitative analysis, characteristic absorption bands with frequencies were used: for cyclohexanone, 1710 cm^{-1}; for cyclohexanol, 1050 cm^{-1}. 1.0 g of cyclohexanol and 0.68 g of cyclohexanone were found, corresponding to 33.2 and 22.5% of the initial C_6H_{11} radicals; the molar ratio of the former to the latter was 1.45:1.

Cyclohexene and cyclohexane were determined in the low-boiling fraction (10 g), obtained by distillation of the filtrate (13 g) under vacuum. They were found in equal proportions and, calculated as the initial C_6H_{11} radicals, amounted to 2.5% each. For quantitative analysis, absorption bands with frequencies of 635 cm^{-1} for cyclohexene and 530 cm^{-1} for cyclohexane were used. The olefin content was confirmed by bromide-bromate titration (2.8%).

From the residue (2.5 g) after distillation, 1.5 g of cyclohexylmercury chloride was isolated, m.p. 163-164° (acetone). This compound was confirmed by analysis for the percentage content of mercury and chlorine.

Found, %: Hg 62.67; 62.81; Cl 10.75; 10.68
$C_6H_{11}HgCl$. Calculated, %: Hg 62.86; Cl 11.12

3.35 g of cyclohexylmercury chloride was found (70.1% of the initial DChM).

Oxidation of DChM in CCl_4. 9.6 g (0.026 mole) of DChM in 25 ml (0.26 mole) of CCl_4 was oxidized at room temperature for 30 h. From the solu—

soon a white crystalline precipitate of cyclohexylmercuric chloride and a small amount of mercury separated from the solution. From the reaction mixture, 0.26 g (5% of the initial amount) of mercury and 6.34 g (76% of the initial amount of DCM) of $C_6H_{11}HgCl$ were isolated. In the filtrate, an insignificant amount of unoxidized DCM was found. The content of cyclohexanol and cyclohexanone was determined by the indicated method, using the characteristic absorption bands with frequencies for $C_6H_{10}O$—1715 cm^{-1}, and for $C_6H_{11}OH$—1075 cm^{-1}. 0.52 g of $C_6H_{11}OH$ and 0.48 g of $C_6H_{10}O$ were found, which amounts to 10% yield each, calculated on the initial C_6H_{11}-radicals. Cyclohexene and cyclohexane were determined in the low-boiling fraction. Their content amounted to 2% each, calculated on the initial C_6H_{11}-radicals. The same content (2%) of olefin was obtained by bromate-bromide titration.

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