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1964

SovietRxiv

Abstract

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A NEW METHOD FOR OBTAINING DIHALOMETHYL ORGANOMERCURY COMPOUNDS

Earlier we described [1] a method for the synthesis of trichloro- and tribromomethyl organomercury compounds by the interaction of organomercury salts $R\text{—}Hg\text{—}X$ with chloroform (bromoform) and potassium tert-butoxide:

$$\mathrm{RHg{—}X + CHX_3 + (CH_3)_3COK \rightarrow RHg{—}CX_3 + KX + (CH_3)_3COH.}$$

In the present work we report the synthesis of dihalomethyl organomercury compounds by the interaction of organomercury salts with methylene chloride or bromide and potassium tert-butoxide according to the general scheme:

$$\mathrm{RHg{—}X + CH_2X_2 + (CH_3)_3COK \rightarrow RHg{—}CHX_2 + KX + (CH_3)_3COH.}$$

The reaction mechanism*, apparently, consists in the fact that monohalocarbenes, generated from methylene chloride and bromide, insert into the $Hg\text{—}X$ bond with formation of dichloro- and dibromomethyl organomercury compounds**:

$$\mathrm{RHg{—}X + :CHX \rightarrow RHg{—}CHX{—}X.}$$

Table 1

$RHgCHX_2$	Yield, %	m.p., °C
$C_6H_5HgCHCl_2$	70	71–72.5
n-$CH_3OC_6H_4HgCHCl_2$	65	89.5–91
-$C_{10}H_7HgCHCl_2$	77	134–135
$C_6H_5HgCHBr_2$	20	84.5–86.5
n-$CH_3OC_6H_4HgCHBr_2$	30	87–89
-$C_{10}H_7HgCHBr_2$	17	118.5–120

In all cases the products were obtained with an admixture of the corresponding symmetrical organomercury compounds, which greatly complicated purification. The synthesized compounds are presented in Table 1.

Some properties of the compounds obtained were studied. When dichloromethyl compounds are treated with an alcoholic solution of hydrogen chloride and with a solution of bromine in CCl_4, cleavage of the bond between mercury and the aromatic ring occurs:

$$\mathrm{R{-}\!\!{-}Hg{-}\!\!{-}CHCl_2 + HCl \rightarrow RH + CHCl_2HgCl} \tag{1}$$

$$\mathrm{C_6H_5{-}\!\!{-}Hg{-}\!\!{-}CHCl_2 + Br_2 \rightarrow C_6H_5Br + CHCl_2HgBr} \tag{2}$$

Apparently, the same bond is also cleaved under the action of sublimate.

$$\mathrm{C_6H_5{-}\!\!{-}Hg{-}\!\!{-}CHCl_2 + HgCl_2 \rightarrow C_6H_5HgCl + CHCl_2HgCl} \tag{3}$$

Phenylation of the chlorodichloromethylmercury formed in reactions (1) and (2) with phenylboronic acid again leads to phenyldichloromethylmercury.

The action of hydrogen chloride on phenyldichloromethylmercury and phenyltrichloromethylmercury (see [1]) makes it possible to arrange the groups $CHCl_2$, CCl_3, and C_6H_5 in the following order of decreasing electronegativity: $CCl_3 > C_6H_5 > CHCl_2$.

* Recently Seyferth et al. [2], having studied the mechanism of the reaction previously described by us of $RHgX$ with CHX_3 and $(CH_3)_3COK$, came to the conclusion that it involves not dihalocarbenes $:CX_2$, but the trihalomethyl anion CX_3^-: $\mathrm{RHg{-}\!\!{-}X + CX_3^- \rightarrow RHg{-}\!\!{-}CX_3 + X^-}$. Apparently, this conclusion is correct. On the other hand, there is no doubt that the methylene group is capable of inserting into the $Hg{-}\!\!{-}X$ bond in the form of the carbene CH_2: (for example, in the reaction of $RHgX$ with diazomethane). The question of whether monohalocarbenes $:CHX$ or the anions CHX_2^- ($\mathrm{RHg{-}\!\!{-}X + CHX_2^- \rightarrow RHg{-}\!\!{-}CHX_2 + X^-}$) participate in the reaction described by us requires special study. It can only be noted that the reaction described is a case more favorable for a carbene mechanism, since monohalocarbenes in their reactivity are closer to the simplest carbene $:CH_2$, which readily inserts into the $Hg{-}\!\!{-}X$ bond, than are dihalocarbenes.

** The simplest dichloromethyl compounds $CHCl_2HgBr$ and $CHCl_2HgJ$ were obtained by Freidlina and Velichko by direct interaction of $CHCl_2Br$ and $CHCl_2J$ with metallic mercury [3].

Experimental Part

1. Preparation of phenyldichloromethylmercury. To a suspension of 3.1 g (0.01 g-mole) of phenylmercuric chloride in 90 ml of absolute benzene, 2 ml (0.031 g-mole) of methylene chloride was added, and then, gradually, with stirring and cooling with ice water, 3.4 g (0.030 g-mole) of potassium tert-butylate was added. The reaction mixture was stirred for three hours and left overnight. The precipitate (potassium chloride, unreacted phenylmercuric chloride) was filtered off and washed with benzene. After evaporation of the benzene, the crystalline residue, in order to separate it from unreacted phenylmercuric chloride and diphenylmercury, was twice dissolved in benzene and filtered from the undissolved precipitate. After evaporation of the benzene, 2.52 g (70%) of phenyldichloromethylmercury was obtained. After fine crystallization from alcohol and from a mixture of alcohol with benzene, m.p. 71–72.5°.

Found, %: Hg 55.41; 55.24
Calculated, %: Hg 55.52

0.5 g of phenyldichloromethylmercury was dissolved in a minimal amount of methyl alcohol and boiled for 15 min with 10 ml of a solution of HCl in methyl alcohol, containing 0.5 g of HCl in 10 ml of solution. After cooling and concentrating the solution, 0.24 g (54%) of dichloromethylmercuric chloride was isolated. After recrystallization from alcohol, m.p. 156.5–157.5°.

Found, %: C 3.93; 4.03; H 0.50; 0.41; Cl 32.89; 32.95
Calculated, %: C 3.76; H 0.31; Cl 33.23

0.12 g of dichloromethylmercuric chloride was dissolved cold in alcohol. 0.1 g of phenylboric acid and 0.08 g of NaOH were dissolved cold in a small amount of water and diluted with alcohol. Both solutions were heated to boiling and poured together. After cooling, the solution was diluted with water; the precipitated solid was filtered off, dried, and treated with benzene to separate metallic mercury. The crystals isolated after evaporation of the benzene were recrystallized from alcohol. Yield 0.12 g (85%) of $C_6H_5HgCHCl_2$, m.p. 72–73.5°.

Found, %: C 23.30; 23.32; H 1.69; 1.67; Cl 20.05; 19.84; Hg 55.12; 54.97
Calculated, %: C 23.20; H 1.66; Cl 19.61; Hg 55.52

To a solution of 0.3 g of phenyldichloromethylmercury in 1 ml of abs. benzene, an excess of bromine in CCl_4 was added. The precipitate was filtered off and treated with benzene. The residue after evaporation of the benzene was recrystallized from alcohol. Yield of bromodichloromethylmercury 0.2 g (70%), m.p. 167–169°.

Found, %: Hg 55.05; 55.20
Calculated, %: Hg 55.07

1 g of phenyldichloromethylmercury and 0.75 g of sulema were heated in 25 ml of alcohol for 30 min. After cooling, the precipitate of phenylmercuric chloride was filtered off. M.p. 250°. The residue after evaporation of the filtrate was

recrystallized from alcohol. This is dichloromethylmercuric chloride with an admixture of phenylmercuric chloride.

Found, %: 4.37; 4.35; H 0.50; 0.31; Cl 32.52; 32.49; Hg 62.33; 61.96
Calculated, %: 3.76; H 0.31; Cl 33.23; Hg 62.69

Preparation of para-anisyldichloromethylmercury. From 3.2 g (0.01 g-mole) of *p*-anisylmercuric chloride, 2 ml (0.031 g-mole) of methylene chloride, and 3.5 g (0.031 g-mole) of potassium tert-butylate in 90 ml of absolute benzene, under the conditions of the preceding experiment, 2.36 g (65%) of *p*-anisyldichloromethylmercury was obtained. The substance was purified by dissolution in benzene and subsequent fourfold recrystallization from a mixture of alcohol with benzene. M.p. 89.5–91°.

Found, %: C 24.73; 24.78; H 2.10; 2.14; Cl 17.68; 17.65; Hg 50.48; 50.83
Calculated, %: C 24.49; H 2.04; Cl 18.11; Hg 51.28

0.5 g of *p*-anisyl dichloromethylmercury was dissolved in 5 ml of alcohol and boiled with 3 ml of an alcoholic solution of hydrogen chloride for several minutes. After cooling, the solution was diluted with water. The precipitate of chlorodichloromethylmercury was filtered off, dried, and recrystallized from alcohol. Yield 0.34 g (83%), m.p. 157°.

Preparation of β-naphthyl dichloromethylmercury. From 2 g (0.005 g-mole) of β-naphthylmercuric chloride, 1 ml (0.015 g-mole) of methylene chloride, and 1.86 g (0.016 g-mole) of potassium tert-butoxide in 60 ml of absolute benzene, under the conditions described earlier, 1.76 g (77%) of β-naphthyl dichloromethylmercury was obtained. The substance was purified by dissolution in benzene followed by two recrystallizations from a mixture of alcohol and benzene. M.p. 134–135°.

Found, %: C 33.01; 32.96; H 2.12; 2.03; Cl 16.43; 16.20; Hg 48.33; 48.36
Calculated, %: C 32.09; H 1.96; Cl 17.22; Hg 48.73

0.5 g of β-naphthyl dichloromethylmercury was dissolved in 10 ml of alcohol and boiled with 3 ml of an alcoholic solution of hydrogen chloride for several minutes. After cooling, the solution was diluted with water. The precipitate of chlorodichloromethylmercury and naphthalene was filtered off. The naphthalene was removed by steam distillation. 0.1 g (67%) of naphthalene was isolated, m.p. 80–81°. A mixed melting-point test with an authentic sample showed no depression.

The residue in the distillation flask was extracted with ether and benzene. The solvent was evaporated. The chlorodichloromethylmercury was recrystallized from a mixture of alcohol and benzene. Yield 0.23 g (65%), m.p. 156–157°.

Preparation of phenyl dibromomethylmercury. From 3.4 g (0.01 g-mole) of phenylmercuric bromide, 3.5 g (0.02 g-mole) of methylene bromide, and 2.4 g (0.02 g-mole) of potassium tert-butoxide in 40 ml of absolute benzene, with cooling by ice water, 0.88 g (20%) of phenyl dibromomethylmercury was obtained.

After four recrystallizations from alcohol, m.p. 84.5–86.5°. The substance could not be obtained in an analytically pure state.

Preparation of para-anisyl dibromomethylmercury. From 4.1 g (0.01 g-mole) of *p*-anisylmercuric bromide, 3.5 g (0.02 g-mole) of methylene bromide, and 2.3 g (0.02 g-mole) of potassium tert-butoxide in 40 ml of absolute benzene at room temperature, 1.52 g (30%) of *p*-anisyl dibromomethylmercury was obtained. The substance was purified by dissolution in benzene followed by two recrystallizations from a mixture of alcohol and benzene. M.p. 87–89°.

Found, %: C 20.53; 20.45; H 1.73; 1.75; Hg 41.57; 41.44
Calculated, %: C 19.96; H 1.66; Hg 41.79

6. Preparation of α-naphthyl dibromomethylmercury. From 4.1 g (0.01 g-mole) of α-naphthylmercuric bromide, 3.5 g (0.02 g-mole) of methylene bromide, and 2.3 g (0.02 g-mole) of potassium tert-butoxide in 40 ml of absolute benzene, with cooling by ice water, 0.84 g (17%) of α-naphthyl dibromomethylmercury was obtained. After two recrystallizations from a mixture of alcohol and benzene, m.p. 118.5–120°.

Found, %: Hg 39.51; 39.74; 40.19
Calculated, %: Hg 40.12

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Received
26 IX 1963

CITED LITERATURE

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