SYNTHESIS AND SOME PROPERTIES OF MERCURY PENTACHLORO- AND PENTABROMOBENZYL COMPOUNDS

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Pentahalobenzyl anions $C_6X_5CH_2^-$ are interesting for experimental study due to the fact that it is difficult to predict in advance how either reactivity or thermodynamic stability will change with change in the nature of the halogen in the series X = F, Cl, Br. All of the halogens below to the (–I, +M) substituents, i.e., they are σ acceptors and π donors, but the ratio of the oppositely directed –I and +M effects is its own for each halogen and, in addition, it should depend on the susceptibility to the indicated effects of the "remaining portion" of the anion.

Organomercury compounds (OMC) are stable potential sources of such carbanions; they are capable of entering into various reactions for the transfer of carbanions from the Hg cation to other electron-deficient electrophilic reagents (S_E reaction). Hg pentafluorobenzyl compounds have been described quite well [1], but the pentachloro- and pentabromobenzylmercury compounds are unknown. Methods for the synthesis and the most characteristic properties of the last two types of OMC are reported in the present paper.

We were unable to synthesize $C_6Cl_5CH_2HgBr$ and $C_6Br_5CH_2HgBr$ (I) the same as $C_6F_5CH_2HgBr$ [1] from the corresponding pentabromo- and pentachlorobenzyl bromides via the Grignard reaction. It proved that pentabromobenzyl bromide fails to react with Mg in either THF or ether when initiated with iodine, while pentachlorobenzyl bromide, although it does react, but after dissolving the Mg and adding the $HgBr_2$ (in THF or ether) the OMC cannot be isolated, while decachlorodibenzyl and a small amount of pentachlorotoluene are formed.

$$C_6Cl_5CH_2Br \xrightarrow[3.\ H_3O^+]{1.\ Mg \quad 2.\ HgBr_2} (C_6Cl_5CH_2)_2 + C_6Cl_5CH_3$$

A change in the reaction conditions (high dilution, lowering the temperature, the use of especially pure Mg, and also the use of EtMgBr instead of Mg metal) did not change the result. When the reaction $C_6Br_5CH_2Br$ with a fourfold excess of Mg is initiated by a double excess of 1,2-dibromoethane the Mg dissolves, but only decabromodibenzyl is formed as a reaction result.

The synthesis of (I) could be accomplished by the direct reaction of a benzene solution of pentabromobenzyl bromide with Hg metal:

$$C_6Br_5CH_2Br + Hg \xrightarrow[20^\circ]{\text{Benzene}} \underset{\text{(I)}}{C_6Br_5CH_2HgBr}$$

Pentachlorobenzyl bromide does not react with Hg under these conditions in 600 h. Irradiation with UV light, frequently used to effect the insertion of Hg across a C–halogen bond (for example, to obtain p-nitrobenzylmercury bromide [2]), leads to the formation of decachlorodibenzyl in the given case.

$$C_6Cl_5CH_2Br + Hg \xrightarrow{h\nu} C_6Cl_5CH_2CH_2C_6Cl_5 \quad (\sim 30\%)$$

It is known that even primary alkyl halides become capable of inserting the Hg atom across the C–halogen bond, provided that anions, which have a high affinity toward Hg (I^-, Br^-, SCN^-, etc.) [3, 4], are added as a catalyst to the system. We used a solution of Et_4NBr as such catalyst. However, organomercury bromides are not formed when catalysis is by bromide

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ions in the case of both $C_6Cl_5CH_2Br$ and $C_6Br_5CH_2Br$, and instead the complete OMC (II) and (III) are formed:

$$2C_6Br_5CH_2Br + 2Hg(Et_4NBr) \xrightarrow[20^\circ]{DMF} \underset{(II)}{(C_6Br_5CH_2)_2 \cdot Hg(100\%)} + HgBr_2$$

$$2C_6Cl_5CH_2Br + 2Hg(Et_4NBr) \xrightarrow[20^\circ]{DMF} \underset{(III)}{(C_6Cl_5CH_2)_2Hg(78\%)} + HgBr_2$$

A very simple explanation for this is that bromide ions not only catalyze the reaction, but they are also symmetrizing agents. For example, the symmetrization of p-$NO_2C_6H_2CH$ HgBr when treated with NaI is described [5].

All of the three obtained Hg polyhalobenzyl compounds are very difficultly soluble in all solvents (in DMF the solubility is $\leqslant 2 \cdot 10^{-4}$ mole/liter). The symmetrical OMC are light-sensitive, especially (III), which deposits Hg completely when exposed to UV light for 5 min.

$$(III) \xrightarrow{h\nu} C_6Cl_5CH_2CH_2C_6Cl_5 + Hg$$

The pyrolysis of solid samples of (II) and (III) at 250-300°C in an ampul for 30 min does not give decahalodibenzyls, like in the case of photochemical decomposition, but mainly pentahalotoluenes. A similar fragmentation is described in the literature during the pyrolysis of dimethylmagnesium [6]: $(CH_3)_2Mg \rightarrow CH_4 + CH_2 = Mg$, which results in the formation of methane and polymeric methylenemagnesium. By analogy with this, the following scheme can be written for the pyrolysis of our compounds.

$$n(C_6X_5CH_2)_2Hg \rightarrow nC_6X_5CH_3 + (C_6X_5CH = Hg)_n$$
$$X = Cl, Br$$

The data on the pyrolysis of polyhalobenzyl compounds will be described in detail in a special communication.

EXPERIMENTAL

Pentabromobenzylmercury Bromide (I). A mixture of 2 g (3.54 mmoles) of $C_6Br_5CH_2Br$ [7], 5 g (24.9 mmoles) of Hg metal, and 50 ml of benzene was shaken in a sealed ampul at ∿20°. The separation of a finely crystalline precipitate became noticeable after 36 h, and its formation was complete in 60 h. After separating the precipitate, the starting bromide was detected in the benzene layer. The precipitate was washed in succession with acetone (300 ml), $CHCl_3$ (200 ml), EtOH (30 ml), and ether (20 ml), and then it was extracted with hot DMF until only Hg metal remained on the bottom of the flask. The hot extract was filtered, cooled, 100 ml of water was added, and the thus obtained white bulky precipitate was filtered on a No. 3 glass filter, washed with acetone, and dried in vacuo over $CaCl_2$. We obtained 1.1 g (40.5%) of (I), mp 263-265° (decomp.). Found: C 11.77; H 0.38; Br 63.82; Hg 24.54%. $C_7H_2Br_6Hg$. Calculated: C 10.97; H 0.27; Br 62.59; Hg 26.17%.

Compound (I) is insoluble or difficultly soluble in all organic solvents. Hg metal was deposited when a solid sample of (I) was irradiated with an Hg lamp for 2 h and other visible changes were not observed.

Bis(pentabromobenzyl)mercury (II). A mixture of 1.8 g (3.18 mmoles) of $C_6Br_5CH_2Br$, 5 g (24.9 mmoles) of Hg metal, and 20 ml of a 0.08 M solution of Et_4NBr in DMF was shaken for 5 h in a sealed ampul. A precipitate started to deposit within 4 min after preparing the reaction mixture. At the end of reaction the precipitate was filtered, and then it was washed in succession with DMF, $CHCl_3$, acetone, benzene, dioxane, EtOAc, and ether (100-ml portions of each solvent) to give 19 g (100%) of (II), mp 255-257° (decomp.). Found: C 14.20; H 0.37; Br 68.40; Hg 17.26%. $C_{14}H_4Br_{10}Hg$. Calculated: C 14.35; H 0.34; Br 68.19; Hg 17.11%. When the $C_6Br_5CH_2Br$ concentration is decreased by 1.5 times the yield of (II) drops to 88%. Replacing the Et_4NBr by NaBr and Et_4NI does not affect the yield of (II).

Compound (II) is even more difficultly soluble in organic solvents than (I). When (II) is exposed to UV light it slowly decomposes with the liberation of Hg metal.

Bis(pentachlorobenzyl)mercury (III). A mixture of 0.2 g (0.58 mmole) of $C_6Cl_5CH_2Br$, synthesized the same as $C_6Br_5CH_2Br$ [7], 2 g (9.97 mmoles) of Hg metal, and 10 ml of an 0.08 M solution of Et_4NBr in DMF was shaken in a sealed ampul for 10 h. A precipitate began to deposit within 1 h. It was filtered and then washed the same as in the described synthesis of (II) to give 0.13 g (61%) of (III) with mp 244-247° (decomp.). Found: C 23.11; H 0.68; Cl 48.99; Hg 27.12%. $C_{14}H_4Cl_{10}Hg$. Calculated: C 23.12; H 0.55; Cl 48.75; Hg 27.57%.

Compound (III) is light-sensitive: In daylight the initially white substance darkens after several hours, while when exposed to UV light in a quartz test tube it becomes black within 5 min. Compound (III) can be stored indefinitely at room temperature in a light-impervious dry box.

An increase in the $C_6Cl_5CH_2Br$ concentration in solution leads to a decrease in the reaction time and an increase in the yields. For example, a mixture of 0.9 g of $C_6Cl_5CH_2Br$, 5 g of Hg, and 20 ml of an 0.08 M solution of Et_4NBr in DMF, with shaking for 3 h, gives 0.75 g (78%) of (III). In the absence of Et_4NBr, $C_6Cl_5CH_2Br$ fails to react with Hg metal even in 600 h, while when shaken in a quartz ampul, with irradiation by an Hg lamp, a mixture of 5 g of Hg and 1.3 g of $C_6Cl_5CH_2Br$ in 20 ml of DMF, C_6H_6, $CHCl_3$, and CCl_4 gives after 60 h 0.8 g (30%) of decachlorodibenzyl, mp 313-315°. Found: C 31.86; H 1.11; Cl 66.97%. $C_{14}H_4Cl_{10}$. Calculated: C 31.92; H 0.77; Cl 67.31%.

CONCLUSIONS

1. The reaction of pentabromo- and pentachlorobenzyl bromides with Hg metal in either DMF or alcohol, catalyzed by halide ions, gave the corresponding bis(pentahalobenzyl)mercury compounds. In the absence of the catalyst anion, pentachlorobenzyl bromide does not react with Hg, while pentabromobenzylmercury bromide is formed from pentabromobenzyl bromide.

2. The pyrolysis of the symmetrical mercury pentabromo- and pentachlorobenzyl compounds gives the corresponding pentahalotoluenes and not the decahalodibenzyls.

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