SYNTHESIS AND PROPERTIES OF TRICHLOROMETHYL- AND
3,3-DICHLOROALLYLMERCURY COMPOUNDS

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In recent years we have studied the chemical transformations of trichloromethyl and 2,2-dichlorovinyl groups in polychlorohydrocarbons and related compounds,* and we considered it to be of interest to find methods of synthesis of organomercury compounds containing these groups and to study their properties. In particular, these compounds could be used for the preparation of other heteroorganic compounds of this type. It is of interest also to study the properties of the \( \text{CCl}_3^+ \) and \( \text{CCl}_2=\text{CHCH}_2^- \) radicals generated by the decomposition of organomercury compounds of this structure (cf., e.g., [2]).

It should be noted that, although organomercury compounds containing the trifluoromethyl group have been prepared [3], attempts to synthesize the trichloromethyl compounds have not been successful. Thus, by the thermal decarboxylation of mercuric trichloroacetate Kharasch and Staveley [4] obtained calomel instead of the expected bistrichloromethylmercury. An attempt to prepare trichloromethylmercury chloride from carbon tetrachloride and mercury under ultraviolet irradiation was also unsuccessful [5].

Trifluoromethylmercury halides and bistrifluoromethylmercury, which were synthesized by Emeleus and Haszeldine [3], approach inorganic salts of mercury in some of their properties: they are soluble in water, and their aqueous solutions conduct electricity. When treated with the usual symmetrizing agents (KI, Na/Hg, Na$_2$S$_2$O$_3$), trifluoromethylmercury halides do not give bistrifluoromethylmercury, but are decomposed with formation of fluoroform. Trifluoromethylmercury compounds, like HgCl$_2$, appear to be able to add at a double bond. Thus, Haszeldine [6] noted that ultraviolet irradiation of a mixture of CF$_3$I and C$_2$H$_4$ at 180° in presence of mercury gives CF$_3$CH$_2$CH$_2$HgI, though in very low yield.

As yet, no 3,3-dihaloallylmercury compound has been described in the literature.

Vigorous agitation of a mixture of CCl$_3$Br and mercury under the irradiation of a PRK-4 mercury lamp in the cold, though better at 70-80°, gave trichloromethylmercury bromide in 41% yield. Addition of a little 2,2'-azobis[2-methylpropionitrile] to the reaction mixture increased the yield of CCl$_3$HgBr. Without irradiation reaction did not go at room temperature and gave only a 7.3% yield of CCl$_3$HgBr at 70-80° in presence of the azo dinitrile. However, when the reaction was carried out in a quartz test tube with simultaneous irradiation, heating, and addition of catalyst, the amount of by-product polymeric and inorganic mercury compounds formed was greatly increased and the yield of trichloromethylmercury bromide was affected unfavorably.

Treatment of CCl$_3$HgBr with moist silver oxide gave trichloromethylmercury hydroxide. When an alcoholic solution of this compound was acidified with 2 N HCl or HI and then diluted with water, CCl$_3$HgCl or CCl$_3$Hgl** were precipitated. The precipitation of CCl$_3$HgCl was incomplete owing to the appreciable solubility of this compound in water. CCl$_3$HgCl and CCl$_3$HgBr are quite stable and do not decompose with keeping; CCl$_3$HgI gradually decomposes with formation of HgI$_2$, particularly in the light. Trichloromethylmercury halides give complexes with pyridine. In the case of CCl$_3$HgI the pyridine complex is unstable and rapidly decomposes with keeping.

Reaction between CCl$_3$HgBr and (C$_6$H$_5$)$_2$SnCl$_2$ takes various courses according to the amount of alkali taken

* For a review of these investigations see [1].
** CCl$_3$HgI can be prepared also by simply shaking CCl$_3$I with mercury in the cold, in spite of Besson's assertion [7], namely, that CCl$_3$I is completely decomposed by mercury in the course of a few hours with liberation of I$_2$ and formation of C$_2$Cl$_4$.
for reaction. When the relative amounts of reactants were stoichiometric in accordance with Equation (1), we obtained phenyl(trichloromethyl)mercury:

$$2CIClHgBr + (C_6H_5)_2SnCl_2 + 6NaOH \rightarrow 2C_6H_5HgCCl_3 +$$
$$+ Na_2SnO_3 + 2NaCl + 2NaBr + 3H_2O; \quad (1)$$

With a 100% excess of alkali, diphenylmercury was obtained. With methanolic HCl, phenyl(trichloromethyl)mercury gave C_6H_5HgCl in quantitative yield, which indicates that the electronegativity of the trichloromethyl group is greater than that of the phenyl group.

An attempt to synthesize phenyl(trichloromethyl)mercury by the photochemical decarboxylation of C_6H_5HgOCOCCl_3 was not successful. After ultraviolet irradiation of methanolic C_6H_5HgOCOCCl_3 for eight hours, phenylmercury chloride and unchanged C_6H_5HgOCOCCl_3 were isolated from the reaction mixture.

Treatment of a chloroform solution of CCl_2HgCl with dry ammonia did not give bistrichloromethylmercury; all the mercury came out of solution in the form of infusible precipitate:

$$\text{Hg} + \text{NH}_3 \rightarrow \text{Hg} + \text{CCl}_2\text{NH}_2 \quad (2)$$

Even in the cold, mercuric sulfide was precipitated quantitatively when alcoholic solutions of CCl_2HgBr were treated with hydrogen sulfide. Reaction between CCl_2HgBr and AgNO_3 was almost instantaneous in slightly warm alcoholic solution, all the bromine present in the CCl_2HgBr being precipitated as AgBr by Ag^+. The trichloromethyl group does not remain inert to AgNO_3, and yields all its chlorine in presence of excess of the reagent. Excess of silver oxide acts similarly on trichloromethylmercury bromide. Treatment of trichloromethylmercury halides with the usual symmetrizing agents (KI, Na_2S_2O_3, Cu) does not give bistrichloromethylmercury.

These facts differentiate trichloromethylmercury compounds from the usual organomercury compounds and indicate their resemblance to inorganic salts of mercury. It is known that pyridine complexes are formed by only a few organomercury compounds of salt-like character, namely quasicomplex compounds [8, 9] and some others (see e.g. [10]). Finally, the reactions of trichloromethylmercury halides with NH_3 and H_2S are highly reminiscent of similar reactions of mercuric chloride. Comparison of trichloromethylmercury compounds with their fluorine analogs indicates that the CCl_3 group is less stable than CF_3.

3,3-Dichloroallylmercury iodide was prepared by direct reaction of CCl_2 - CHCH_2I with mercury. At room temperature without irradiation reaction was rather slow and yields did not exceed 44%. In a wide-mouthed quartz test tube with irradiation by a PRK-4 mercury lamp, reaction was complete within 30 minutes and the yield of CCl_2 - CHCH_2HgI was 67%. This product is unstable and decomposes on keeping with separation of HgI_2. Treatment of an alcoholic solution of 3,3-dichloroallylmercury iodide with moist silver oxide and subsequent treatment with 2 N HCl or 2 N HBr gave CCl_2 - CHCH_2HgBr or CCl_3 - CHCH_2HgCl.

Neither CCl_2 - CHCH_2HgI nor CCl_2 - CHCH_2HgCl behaves as a conjugated system (see e.g. [11]) in reaction with maleic anhydride. These compounds do not react with benzoyl chloride with formation of ketones. When CCl_2 - CHCH_2HgI was treated with C_6H_5COCl, no ketone was formed; a resinous reaction mixture was obtained, and from this, by chromatography on alumina, we isolated CCl_2 - CHCH_2HgCl, HgI_2, HgCl_2, and unchanged CCl_2 - CHCH_2HgI and C_6H_5COCl. In this reaction the behavior of CCl_2 - CHCH_2HgI is reminiscent of that of its allyl analog [12].

**EXPERIMENTAL**

1,1-Dichloro-3-iodopropene. To a solution of 30 g (0.2 mole) of NaI in 150 ml of acetone, 30 g (0.2 mole) of CCl_2CH = CH_2 was added and the mixture was boiled in a water bath for 90 minutes. The reaction product was then poured into water, and the lower layer was separated, washed with sodium thiosulfate solution and with water, dried over sodium sulfate, and vacuum-distilled. A fraction of b.p. 68-70° (10 mm) (19.7 g) was collected. Redistillation gave 18.2 g (34%) of CCl_2 - CHCH_2I*, b.p. 63° (8 mm); n^20_D 1.6020; d^20_4 2.0320.

* Compare [13].