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Abstract

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SYNTHESIS AND CHEMICAL TRANSFORMATIONS OF TRICHLOROMETHYL AND ω,ω-DICHLOROALLYL MERCURY COMPOUNDS

Since organomercury compounds containing trichloromethyl or dichloroallyl groups are of interest from the standpoint of studying the chemical behavior of these groups, we investigated the possibility of synthesizing such compounds and studied some of their transformations.

Whereas organomercury compounds containing trifluoromethyl (^{1}) or triiodomethyl (^{2}) groups have been described, attempts to synthesize trichloromethyl compounds by decarboxylation of mercury trichloroacetate (^{3}) or by the photochemical reaction of carbon tetrachloride with mercury (^{4}) remained unsuccessful.

Not a single representative of ω,ω-dihaloallyl organomercury compounds has been described in the literature up to the present time.

We studied the reactions of bromotrichloromethane, bromo- and iododichloromethane, and 1,1-dichloro-3-iodopropene-1* with mercury under illumination with UV light of a reaction mixture heated to 70–80° and vigorously stirred, as well as the reaction of iodotrichloromethane with mercury upon simple shaking of these reagents without illumination. The following compounds were thereby obtained: CCl_3HgBr, $CHCl_2HgBr$, $CHCl_2HgJ$, $CCl_2{=}CHCH_2HgJ$, and CCl_3HgJ, in yields, respectively, of 41; 1.2; 2.5; 67; and 12% of theory.

In the interaction of bromotrichloromethane with the calculated amount of 0.5% sodium amalgam, along with hexachloroethane, trichloromethylmercury bromide was also obtained in small yield, and not the symmetrical compound $(CCl_3)_2Hg$. An anomaly of this kind is known only for iodocyclohexylmercury (^{5}).

In contrast to chloromethylmercury halides, which decompose under the action of alkalis with liberation of mercury (^{6}), trichloromethylmercury bromide, when treated with moist silver oxide, is converted into the comparatively stable trichloromethylmercury hydroxide. By careful neutralization of an aqueous solution of CCl_3HgOH with hydrochloric or hydroiodic acid, CCl_3HgCl and

CCl_3HgJ were obtained. By the same route, the chloride and bromide were obtained from $CCl_2{=}CHCH_2HgJ$.

We have also found an even simpler and more convenient method of converting alkylmercury iodides into chlorides, consisting in an exchange reaction with sublimate upon heating in ether or alcohol. The reaction proceeds according to the scheme:

$$2RHgJ + HgCl_2 \rightarrow 2RHgCl + HgJ_2$$

In a number of reactions trichloromethyl mercury compounds resemble the so-called "quasicomplex" compounds. Trichloromethylmercury halogenides give complexes with pyridine, as do "quasi-complex"compounds (7,ζ). In the case of CCl_3HgJ the complex is unstable and, on storage, rapidly decomposes.

When dry ammonia is passed into a chloroform solution of CCl_3HgCl, bistrichloromethylmercury is not formed; instead, a nonmelting precipitate is formed in 95.5% yield:

$$ClHgCCl_3 + NH_3 \rightarrow ClHgNH_2 + CHCl_3$$

Ammonium chloride was not detected in the reaction mixture.

Hydrogen sulfide, even in the cold, quantitatively liberates HgS from an alcoholic solution of trichloromethylmercury bromide.

The reactions of trichloromethylmercury bromide with C_6H_5MgBr and $(C_6H_5)_2SnCl_2$ also proceed in a distinctive manner.

On interaction of trichloromethylmercury bromide with C_6H_5MgBr under the usual conditions for obtaining unsymmetrical organomercury compounds (9), phenyltrichloromethylmercury was obtained along with phenylmercury bromide. A similar exchange of radicals between RHgX and R′MgX with formation of R′HgX and RMgX has been noted only in a few cases (10–12).

The interaction of trichloromethylmercury bromide with diphenyldichlorostannane under the usual conditions (13) proceeds in different directions depending on the amount of alkali taken into the reaction. With a stoichiometric ratio of reagents, in accordance with the equation:

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* Obtained from $CCl_3{-}CH{=}CH_2$, and also from $CCl_2{=}CHCH_2Cl$ by exchange reaction with NaJ in acetone, b.p. 69-70°/10 mm.

Found, %: C 15.29; 15.20; H 1.39; 1.57
Calculated, %: C 15.21; H 1.28.

$$2CCl_3HgBr + (C_6H_5)_2SnCl_2 + 6NaOH \rightarrow$$
$$\rightarrow 2CCl_3HgC_6H_5 + Na_2SnO_3 + 2NaCl + 2NaBr + 3H_2O$$

phenyltrichloromethylmercury was obtained in 49% yield. With a larger amount of alkali the reaction proceeds with formation of diphenylmercury (29%), apparently according to the equation:

$$CCl_3HgBr + (C_6H_5)_2SnCl_2 + 5NaOH \rightarrow$$
$$\rightarrow (C_6H_5)_2Hg + Na_2SnO_3 + 2NaCl + NaBr + CHCl_3 + 2H_2O$$

In both cases, considerable formation of nonmelting and insoluble precipitates containing mercury was observed.

With methanolic HCl, phenyltrichloromethylmercury quantitatively forms C_6H_5HgCl, which indicates the greater relative electronegativity of the trichloromethyl group as compared with the phenyl group. On heating phenyltrichloromethylmercury for half an hour in a sealed ampoule at 150°, C_6H_5HgCl is formed (80%):

$$2C_6H_5HgCCl_3 \rightarrow 2C_6H_5HgCl + CCl_2 = CCl_2$$

In an attempt to synthesize phenyltrichloromethylmercury by photochemical decarboxylation at ordinary temperature, $C_6H_5HgOCOCCl_3$ (obtained from C_6H_5HgOH and CCl_3COOH) in methanol gave, from the reaction mixture, along with unreacted product, only phenylmercury chloride.

An analogous result was obtained on heating $C_6H_5HgOCOCCl_3$ in vacuum to 240° for several minutes.

The action of ordinary "symmetrizers"(KJ, $Na_2S_2O_3$, Cu) on trichloromethylmercury halides does not lead to formation of bistrichloromethylmercury.

The analytical data and melting points of the synthesized organomercury compounds are given in Table 1.

Table 1

Compound	M.p., °C	Found, %	Calculated, %
CCl_3HgBr	165	C 3,10; 3,25; Cl 26,78; 26,69; Br 20,03; 20,23	C 3,03; Cl 26,68; Br 20,03
$CCl_3HgBr \cdot C_5H_5N$	87	C 15,15; 14,91; H 0,87; 0,81; Cl 22,08; 22,00; Br 16,57; 16,55	C 15,07; H 1,05; Cl 22,25; Br 16,72

Compound	M.p., °C	Found, %	Calculated, %
CCl_3HgJ	117	C 2,85; 2,93; Cl 23,42; 23,92	C 2,69; Cl 23,85
CCl_3HgCl	173	C 3,29; 3,16; Hg 56,90	C 3,39; Hg 56,60
CCl_3HgOH	175	C 3,91; 4,00; H 0,02; 0,05; Cl 31,66	C 3,57; H 0,30; Cl 31,65
$CCl_3HgC_6H_5$	116	C 20,84; 21,02; H 1,13; 1,22; Cl 26,11; 26,43	C 21,23; H 1,27; Cl 26,79
$CHCl_2HgBr$	152	C 3,36; 3,24; H 0,23; 0,28; halide 40,98	C 3,30; H 0,28; halide 41,39
$CHCl_2HgJ$	130	C 2,49; 2,59; H 0,32; 0,31	C 2,92; H 0,24
$CCl_2{=}CHCH_2HgJ$	46	C 8,80; 8,85; H 0,72; 0,64; Cl 16,97; 17,04	C 8,23; H 0,69; Cl 16,20
$CCl_2{=}CHCH_2HgBr$	94,5	C 8,67; 8,73; H 0,79; 0,77	C 9,23; H 0,77
$CCl_2{=}CHCH_2HgCl$	100	C 10,17; 10,39; H 0,94; 1,13	C 10,41; H 0,87
$C_6H_5HgOCOCCl_3$	240	C 21,46; 21,43; H 1,10; 1,27; Hg 45,52; 46,05	C 21,60; H 1,15; Hg 45,35
$CCl_2{=}C(CH_3)CH_2HgJ$*	101	C 10,65; 10,78; H 1,02; 0,98	C 10,64; H 1,12
$CCl_2{=}C(CH_3)CH_2HgBr$	109	Br 20,30; 20,43	Br 19,75
$CCl_2{=}C(CH_3)CH_2HgCl$	127	Cl 29,69; 29,56	Cl 29,54

* Obtained from 1,1-dichloro-2-methyl-3-iodopropene-1, b.p. 77°/10 mm.

Found, %: C 19,49; 19,49; H 2,05; 2,02
Calculated, %: C 19,15; H 2,01

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