PENTACHLOROPHENYL ORGANOMERCURY COMPOUNDS

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Current interest in pentafluorophenyl-metal compounds[1-5] and the effect of electron-withdrawing groups on the stability of carbon-metal bonds[6] prompted this investigation of the preparation and properties of some pentachlorophenylmercury compounds.

Pentachlorophenylmagnesium chloride may be prepared directly from hexachlorobenzene and magnesium in tetrahydrofuran[7]. This Grignard reagent can only be prepared in diethyl ether if an entrainment method using 1,2-dibromoethane is employed[8]. Preparations of bis(pentachlorophenyl)mercury in essentially the same yields were observed whether diethyl ether or tetrahydrofuran was used as the solvent in the reaction with $HgCl_2$.

The pentachlorophenylmercury compounds were found to have great thermal stability similar to that found for the pentafluorophenyl derivatives. Thus, bis(pentachlorophenyl)mercury melts at 383°, compared to the value of 142° reported for the fluoro derivative.

Unsymmetrical derivatives of this parent compound may be prepared by prolonged heating at temperatures above 200° of this compound with another organomercury compound. The unsymmetrical compounds, however, disproportionate in a boiling solution in diethylene glycol dimethyl ether. Procedures are listed below for preparation of $C_6Cl_5HgCH_3$ and $C_6Cl_5HgC_6H_5$.

The hydrochloric acid cleavage of (pentachlorophenyl)phenylmercury and (pentachlorophenyl)methylmercury preferentially removes the phenyl and pentachlorophenyl groups respectively, which is consistent with the cleavages of pentafluorophenylmercury compounds, and with the conclusion of Dessy and Kim[9] that cleavage occurs preferentially at the carbon carrying the highest electron density.

It is interesting that although the phenyl and methyl derivatives may be prepared by a redistribution reaction between diphenyl- or dimethylmercury with bis(pentachlorophenyl)mercury, only the phenyl compound may be prepared from the following exchange reaction:

$$C_6Cl_5HgCl + R_2Hg \xrightarrow{\text{benzene}} RHgCl + C_6Cl_5HgR$$

Attempts to prepare the methyl derivative by this method gave an almost quantitative yield of bis(pentachlorophenyl)mercury, presumably through a second exchange

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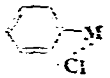
reaction. A reaction analogous to that above has been found useful in the synthesis of a new series of unsymmetrical carbomethoxymercury compounds as follows[10]:

$$ClHgCO_2CH_3 + R_2Hg \xrightarrow{\text{solvent}} RHgCl + CH_3O_2CHgR$$

The driving force for this reaction is the precipitation of the organomercury halide and it was found necessary to change solvents in order to prepare certain derivatives. This may be true in the former case also.

These compounds are reported in the hope that they may stimulate further work in this area. The fashionable nature of fluorine chemistry has led to the neglect of C_6Cl_5–M systems. The ease of preparation, cost differential, and possibility for



interactions should make it a profitable area.

EXPERIMENTAL

Analyses for carbon, hydrogen, and chlorine are by Galbraith Laboratories, Inc., Knoxville, Tennessee. Spectra of Nujol mulls of these monosubstituted hexachlorobenzene derivatives indicated a characteristic sharp and intense absorption in the range 845–855 cm^{-1}.

Bis(pentachlorophenyl)mercury, $(C_6Cl_5)_2Hg$

To magnesium turnings (3.0 g, 0.125 mole) in tetrahydrofuran (50 cc) was added 1,2-dibromoethane (0.5 cc) to activate the magnesium. More tetrahydrofuran (200 cc), was then added, followed by hexachlorobenzene (28.5 g, 0.10 mole) in small increments over half an hour. After being stirred for about four hours, the reddish-brown solution obtained was found to contain 70–75 % yield of Grignard reagent as indicated by hydrolysis and titration of the magnesium hydroxide with standard acid solution.

The Grignard solution was decanted from unreacted magnesium and added, over thirty minutes, to excess mercuric chloride (13.6 g, 0.05 mole) dissolved in tetrahydrofuran. The precipitate was filtered off and washed in boiling water (400 cc). The solid was dried and recrystallized from boiling nitrobenzene twice to give white needles (14–15 g, about 50 % yield), m.p. 383°. (Found: C, 20.70; H, 0.21; Cl, 50.41. $C_{12}Cl_{10}Hg$ calcd.: C, 20.61; H, 0.00; Cl, 50.70 %.)

Pentachlorophenylmercuric chloride, C_6Cl_5HgCl

Bis(pentachlorophenyl)mercury (7 g, 0.01 mole) with mercuric chloride (2.7 g, 0.01 mole) in nitrobenzene (50 cc) was refluxed for two hours. The hot solution was filtered and cooled to yield a white solid which was recrystallized from benzene as white needles, m.p. 264°, (8.7 g, 90 % yield). (Found: C, 15.01; H, 0.15; Cl, 43.64. C_6Cl_6Hg calcd.: C, 14.85; H, 0.00; Cl, 43.83 %.)

(Pentachlorophenyl)phenylmercury, $C_6Cl_5HgC_6H_5$

Pentachlorophenylmercuric chloride (4.9 g, 0.01 mole) and diphenylmercury (3.5 g, 0.01 mole) were dissolved in boiling benzene (350 cc). After cooling to 10°, the precipitated white solid was filtered off and dried. This was identified as phenylmercuric chloride (2.5 g, 80% yield) by mixed melting point with an authentic sample. The filtrate was evaporated to dryness *in vacuo* and the solid obtained was dissolved in boiling ligroin (b.p. 90–120°, 300 cc) and filtered. Prolonged boiling was avoided in this step. On cooling to 0°, a white crystalline solid was obtained which recrystallized from benzene as white flaky crystals, m.p. 220° (4.7 g, 89% yield). (Found: C, 27.25; H, 1.16; Cl, 33.38. $C_{12}H_5Cl_5Hg$ calcd.: C, 27.34; H, 0.96; Cl, 33.64%.) This compound may also be prepared by the same method as the (pentachlorophenyl)methyl compound described below.

(Pentachlorophenyl)methylmercury, $C_6Cl_5HgCH_3$

Bis(pentachlorophenyl)mercury (4 g, 5.7 mmoles) and dimethylmercury (1.5 g, 6.5 mmoles) were sealed in a pyrex glass tube under vacuum and then heated in an oil bath at 210–220° until the mixture liquified (about 12 h). The tube was cooled and the liquid froze to a white solid. Recrystallization three times from ethanol gave a white crystalline solid, m.p. 202–3° (3.6 g, 90% yield). (Found: C, 18.15; H, 0.86; Cl, 37.86. $C_7H_3Cl_5Hg$ calcd.: C, 18.08; H, 0.65; Cl, 38.13%.)

Cleavage of (pentachlorophenyl)phenylmercury with hydrogen chloride

Since it had been found that ethereal solvents tended to cause disproportionation of the unsymmetrical compounds, benzene was used as solvents for reactions. Hydrogen chloride was bubbled through benzene for 20 min. Analysis showed that the solution then contained 0.252 moles of hydrogen chloride per litre.

To (pentachlorophenyl)phenylmercury (0.151 g, 0.286 mmole) was added benzene (15 cc) followed by 0.252 *M* HCl in benzene (1.14 cc). The compound dissolved and the solution was allowed to stand for two days. Removal of solvent gave a white solid, m.p. 262–4°, identified as pentachlorophenylmercuric chloride.

Cleavage of (pentachlorophenyl)methylmercury with hydrogen chloride

(Pentachlorophenyl)methylmercury (0.380 g, 0.817 mmole) with benzene (25 cc) was mixed with a 0.252 *M* HCl solution in benzene (3.24 cc) and the solution left standing for two days. On slowly removing the benzene *in vacuo* a first crop of white crystals was obtained, 0.17 g, m.p. 84–5° (lit. pentachlorobenzene, m.p. 86°).

Further removal of solvent afforded a white solid which after recrystallization from ethanol melted at 169° in a sealed tube (lit. methylmercuric chloride, m.p. 170°).

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SUMMARY

The following pentachlorophenyl derivatives of mercury have been prepared; $(C_6Cl_5)_2Hg$, C_6Cl_5HgCl, $C_6Cl_5HgCH_3$ and $C_6Cl_5HgC_6H_5$. Acid attack on the latter two species leads to scission of the C_6Cl_5–Hg and C_6H_5–Hg bonds respectively, in agreement with the C_6F_5–Hg compounds. Like the latter, these pentachlorophenyl deriva-

tives have a very high thermal stability. The ease of preparation and cost-differential compared to the fluorine derivative and the possibility for metal–ring halogen interaction suggest this grouping as deserving of further investigation.

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