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HALOMETHYL-METAL COMPOUNDS

VI*. PHENYL(DIHALOMETHYL)MERCURY COMPOUNDS: THEIR PREPARATION AND SOME CLEAVAGE REACTIONS

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In a previous communication[2] we reported that tri-*n*-butyltin hydride reduced $C_6H_5HgCCl_2Br$, $C_6H_5HgCClBr_2$ and $C_6H_5HgCBr_3$ to the dihalomethylmercurials, $C_6H_5HgCHCl_2$, $C_6H_5HgCHClBr$ and $C_6H_5HgCHBr_2$, respectively. It was noted that these reactions were not of practical utility from the preparative point of view. While these studies were in progress, Reutov and Lovtsova described the extension of their haloform-base procedure for $C_6H_5HgCX_3$ preparation[3] to the synthesis of aryl(dihalomethyl)mercury compounds[4]. Thus the reaction of phenylmercuric chloride with methylene chloride and potassium tert-butoxide gave phenyl(dichloromethyl)mercury (eqn. 1):

$$C_6H_5HgCl + \text{tert-BuOK} + CH_2Cl_2 \rightarrow C_6H_5HgCHCl_2 + KCl + \text{tert-BuOH} \quad (1)$$

Our interest in phenyl(dihalomethyl)mercurials and in their applications in synthesis[2,5,6,7] led us to use this general procedure to prepare all possible chlorine-, bromine- and iodine-containing phenyl(dihalomethyl)mercury compounds, using in each case the appropriate methylene halide. The yields of recrystallized product obtained ranged from moderate (30–40 %) to quite good (up to 75 %).

All six members of the series $C_6H_5HgCHXY$ (X, Y = Cl, Br, I) are crystalline solids which are not appreciably sensitive to light, air or moisture. The dichloro-, dibromo- and bromochloromethylmercurials are colorless, while the iodine-containing compounds always were isolated as light yellow or yellow-green solids. Their characteristic physical properties are listed in Table 1. The infrared spectra of the phenyl(dihalomethyl)mercury compounds contain the expected phenyl, carbon–hydrogen and carbon–halogen bands, with strong peaks between 1050 and 1250 cm^{-1} (C–H vibration) being the most useful for characterizing individual members of the series (Table 1). NMR analysis of these mercurials, a useful means of determining relative amounts of each in mixtures, reveals phenyl (7.2–7.3 δ from TMS) and aliphatic hydrogen peaks (4.5–6.0 δ) in 5:1 integrated ratio. The position of the latter peak corresponds closely in most instances to the δ values predicted from the empirical

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formula based on Dailey and Shoolery's values for hydrogen shielding of methylene protons[8,9]. The effective shielding constants of the halogens, $\sigma(i_{eff})$, were determined by these authors, and comparison of the proton positions in the $C_6H_5HgCHXY$ compounds with those of the related dihalomethanes (given in ref. 8) permitted derivation of a constant for the phenylmercury substituent. The calculated values of the methine proton position agree within 5 % with those observed, but it should be noted that the relative values observed for the chloroiodo- and the dibromomethylmercurials, like those of the corresponding dihalomethanes, are reversed from those predicted.

Reutov and Lovtsova have reported[4] that the phenyl–mercury bond of phenyl(dichloromethyl)mercury is cleaved preferentially by alcoholic hydrogen chloride and by bromine. We found that complete cleavage of both organic groups from the $C_6H_5HgCHXY$ compounds is easily accomplished. Such cleavage, followed by g.l.c. analysis of the volatile products, provides another means of distinguishing these mercurials and is especially useful in the analysis of mixtures of $C_6H_5HgCHXY$ compounds:

$$C_6H_5HgCHXY + 2\,Br_2 \xrightarrow{CCl_4,\,65^\circ} HgBr_2 + C_6H_5Br + CHXYBr \qquad (2)$$

No single solvent (including acetone, chloroform, carbon tetrachloride, diethyl ether, pentane, hexane, methanol, ethanol and benzene) was found in which all six compounds were both stable and soluble. The dibromo-, bromochloro- and dichloromethylmercurials were moderately to very soluble in most of the above-mentioned solvents, but only slightly soluble in the alcohols and aliphatic hydrocarbons. The iodine-substituted mercurials were found to be stable for a length of time sufficient for normal recrystallization procedures only in benzene, methanol, ethanol and aliphatic hydrocarbons. They formed either a purple solution or a flaky solid when dissolved in the other solvents for a short period at room temperature. Concentrated solutions of phenyl(diiodomethyl)mercury decomposed rapidly in hot benzene and over a period of several hours in this solvent at room temperature.

We had shown previously[10] that the formation of $C_6H_5HgCX_3$ compounds by the action of haloform and potassium tert-butoxide on phenylmercuric halide proceeds by way of nucleophilic attack by CX_3^- on mercury, rather than via dihalocarbene insertion into the mercury-halogen linkage. In the present case product formation also occurs by a displacement mechanism:

$$CH_2X_2 + \text{tert-BuOK} \rightarrow K^+ + CHX_2^- + \text{tert-BuOH} \qquad (3)$$

$$CHX_2^- + C_6H_5HgY \rightarrow C_6H_5HgCHX_2 + Y^- \qquad (4)$$

Thus phenyl(dichloromethyl)mercury was the product of the reaction of methylene *chloride*, potassium tert-butoxide and phenylmercuric *bromide*. Bromine cleavage of the product gave only bromodichloromethane and no dibromochloromethane, which demonstrated the absence of $C_6H_5HgCHClBr$. A carbene insertion mechanism would have required formation of the latter in this reaction. As has already been pointed out[10], halogen exchange between phenylmercuric bromide and potassium chloride would complicate this picture, but it was shown not to occur under these conditions. Furthermore, the possibility of initial formation of phenyl(bromochloromethyl)-

TABLE 1

PROPERTIES AND ANALYSES OF PHENYL(DIHALOMETHYL)MERCURY COMPOUNDS

Mercurial	*M.p. (°C)*	*Characteristic C–H vibration (cm⁻¹)*[a]	$\delta(CHX_2)$[b]		*Analysis, found (calcd.) (%)*					
			Predicted[c]	*Observed*	*Carbon*	*Hydrogen*	*Mercury*	*Chlorine*	*Bromine*	*Iodine*
$C_6H_5HgCHCl_2$	71–72	1205	6.10	6.00[f]	23.36 (23.25)	1.93 (1.67)	55.24 (55.47)	19.67 (19.61)		
$C_6H_5HgCHClBr$	67–68	1180	5.99	5.87[f]	20.51 (20.70)	1.77 (1.49)	49.37 (49.40)	8.66 (8.73)	19.99 (19.68)	
$C_6H_5HgCHBr_2$[d]	69–70	1135	5.79	5.73[f]	18.65 (18.66)	1.20 (1.34)	44.56 (44.52)		35.36 (35.48)	
$C_6H_5HgCHClI$	55–56	1175	5.48	5.77[g]	18.28 (18.55)	1.23 (1.34)	44.39 (44.27)	7.37 (7.82)		27.96 (28.01)
$C_6H_5HgCHBrI$	85–86[e]	1120	5.28	5.47[g]	16.78 (16.90)	1.14 (1.21)	40.07 (40.32)		16.08 (16.06)	25.54 (25.51)
$C_6H_5HgCHI_2$	110–111[e] (dec.)	1080	4.77	4.69[g]	15.60 (15.44)	1.22 (1.11)	36.69 (36.84)			46.20 (46.61)

[a] The most useful peak for distinguishing individual members of this series. [b] δ (ppm) downfield from tetramethylsilane. [c] $\tau = 9.767 - \sum_i \sigma(i_{eff})$; $(\delta = 10 - \tau)$. $\sigma(i_{eff})$ for Cl, Br, I, and C_6H_5Hg = 2.53, 2.33, 1.82, 0.90, respectively. *Cf.* refs. 8 and 9. [d] The high-yield preparation of phenyl(dibromomethyl)mercury as a solid with correct analysis and integrated NMR spectrum places in doubt the claim[4] that this mercurial had been prepared in 20% yield as a solid of m.p. 84.5–86.5° for which a correct analysis could not be obtained. [e] Decomposes somewhat on melting. [f] $CDCl_3$ solution, TMS internal standard. [g] CS_2 solution, TMS external standard, cyclohexane internal standard.

mercury, followed by its reaction with chloride ion to produce the observed dichloromethylmercurial, was disproven by the recovery of the former mercurial essentially unchanged from a reaction mixture (standard conditions, *i.e.*, high-speed stirring, toluene slurry, 0°, etc.) with methylene chloride, potassium chloride and tert-butanol. In addition, a reaction between potassium tert-butoxide and CH_2X_2 ($X = Br$ and/or Cl) in the presence of cyclohexene under conditions identical to those used in mercurial preparations produced no 7-halonorcarane, thus placing in doubt the formation of halocarbenoid intermediates in these reactions. This view is further supported by the attempts of Vol'pin and coworkers[11] to prepare tropylium bromide from benzene with methylene halide and potassium tert-butoxide. The desired product, presumably formed via a halocarbene intermediate, was produced in all cases in less than 2 % yield.

We have shown previously that iodide ion readily displaces trihalomethide ion from phenyl(trihalomethyl)mercury compounds under mild conditions (eqn. 5)[12].

$$C_6H_5HgCX_3 + Na^+I^- \xrightarrow{DME} C_6H_5HgI + CX_3^- + Na^+ \tag{5}$$

In the absence of a substrate capable of intercepting the trihalomethide ion, the latter gave dihalocarbene. Thus in the presence of an equimolar amount of sodium iodide, phenyl(trichloromethyl)mercury dichloromethylenated many olefins in high yield within 4 h at 80°. This is in contrast to the 36–48 h reaction times required for high yield synthesis of *gem*-dichlorocyclopropanes using $C_6H_5HgCCl_3$ in the thermal reaction in refluxing benzene.

The success of the iodide ion procedure in the case of phenyl(trichloromethyl)-mercury suggested its possible application in the "activation" of the phenyl(dihalomethyl)mercury compounds, which had been found to be of rather low reactivity in halocyclopropane synthesis at 80°. The study of the action of sodium iodide on phenyl(dihalomethyl)mercurials was made of even greater interest by the report[13] that ethyl(chloromethyl)mercury underwent extremely rapid nucleophilic substitution *at carbon* when treated with sodium iodide in acetone (eqn. 6).

$$C_2H_5HgCH_2Cl + I^- \xrightarrow{acetone} C_2H_5HgCH_2I + Cl^- \tag{6}$$

Thus attack at mercury or at carbon was possible in the case of $C_6H_5HgCHXY$ compounds.

Nucleophilic attack of iodide ion on phenyl(dihalomethyl)mercury compounds occurred at carbon, rather than at mercury:

$$C_6H_5HgCHX_2 + I^- \rightarrow C_6H_5HgCHXI + X^- \tag{7}$$

The reaction of $C_6H_5HgCHClBr$ with one molar equivalent of sodium iodide at 25° resulted in formation of phenyl(chloroiodomethyl)mercury (79 % pure yield) and a quantitative yield of sodium bromide*. This, it should be mentioned, is a much better synthesis of this mercurial than is the $C_6H_5HgX + CH_2ClI +$ tert-BuOK reaction. A similar reaction of sodium iodide with phenyl(dibromomethyl)mercury led to a mixture of unconverted mercurial, phenyl(bromoiodomethyl)mercury and phenyl-(diiodomethyl)mercury. Although small amounts of $C_6H_5HgCHBr_2$ and $C_6H_5HgCHI_2$

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* Initial experiments were carried out in DME/benzene, but methanol/benzene was found to be a better reaction medium in later work.

could be separated by fractional crystallization, the desired $C_6H_5HgCHBrI$ could not be obtained in the pure state by this procedure, even when the reaction was carried out at $-55°$ or with an excess of starting mercury compound. Nucleophilic displacement of both halogens of phenyl(dichloromethyl)mercury and of the dibromomethyl compound was effected with an excess of sodium iodide (at 65° and 25° respectively), to give phenyl(diiodomethyl)mercury in high yield.

Such nucleophilic displacements at carbon in $C_6H_5HgCHXY$ compounds should make possible the preparation of other interesting organofunctional organomercury compounds of type $C_6H_5HgCHXZ$ (X = halogen; Z = some other functional group), which might be useful as CHZ transfer agents. This aspect of dihalomethylmercury chemistry is under active investigation. The preparation, in low yield, of $C_6H_5HgCH(Cl)SCN$, by the action of methanolic sodium thiocyanate on phenyl(bromochloromethyl)mercury is to be noted in this connection.

A subsequent paper will deal with the use of phenyl(dihalomethyl)mercury compounds as halomethylenation agents.

EXPERIMENTAL

General comments

Infrared spectra were recorded on a Perkin Elmer Infracord 237 or 337 spectrophotometer. All mercurials were examined as mulls (Nujol, hexachlorobutadiene) using sodium chloride plates. Proton resonance spectra were obtained with a Varian Associates A60 NMR spectrometer. Chemical shifts are given in ppm downfield from tetramethylsilane. Elemental analyses were performed by Dr. S. M. NAGY, M.I.T. Microchemical Laboratory, the Galbraith Laboratories, Knoxville, Tenn. and the Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

Preparation of phenyl(dibromomethyl)mercury

A one-liter, three necked Morton flask, previously flushed with prepurified nitrogen and fitted with a condenser and heating mantle, was charged with 200 ml of tert-butanol (dried over sodium) and 6.6 g (0.17 g-atom) of potassium. The mixture was heated at reflux overnight. Under a positive pressure of nitrogen, the condenser was removed and the flask was fitted with a distillation head and mechanical stirrer. As the tert-butanol was removed by distillation, 500 ml of dry toluene was added slowly in two increments, and the distillation was continued until the head temperature ceased to rise (*ca.* 109°). The resulting slurry of potassium tert-butoxide in *ca.* 250 ml of toluene was permitted to cool, additional toluene was added to bring the total volume to about 500 ml, and the reaction vessel was fitted with a high-speed stirrer in place of the ordinary mechanical stirrer; the distillation head was removed. Following addition of 26.3 g (0.084 mole) of phenylmercuric chloride, the mixture was chilled (with high-speed stirring) in an ice bath to below 5°; 58.5 g (0.34 mole) of dibromomethane then was added slowly and the resulting mixture stirred for 3 h. The reaction mixture was poured into 400 ml of distilled water with stirring, and after 15 min was filtered from 1.9 g of gray solid. The aqueous and organic phases were separated and washed with two 100 ml portions of toluene and water, respectively. The combined organic phases were dried, filtered and evaporated at reduced pressure. The crude product consisted of a tan oil which slowly crystallized to a colorless solid, m.p. 61–64°, 30.9 g (80 % crude yield). This solid was recrystallized from 175 ml of a 2:1 (by volume) n-hexane-chloroform mixture, resulting in a first crop of 24.5 g (65 %) of colorless needles, m.p. 67–69°. Further crops melted only partially below 70°. An analytical sample had m.p. 68–69°.

Phenyl(bromochloromethyl)mercury and phenyl(dichloromethyl)mercury were prepared by essentially the same procedure, using bromochloromethane and dichloromethane, respectively. Yields of pure product were 63 % and 45 %, respectively. A factor which tended to limit the yields in these reactions was the occurrence of side-reactions which produced diphenylmercury and metallic mercury. The first crops of recrystallized crude material consisted almost entirely of the desired product, but further crops tended to melt above 100°, and recrystallized samples were identified by mixture m.p. and IR spectra as diphenylmercury. The formation of these side-products even in the preparation of the bromochloromethyl- and the dibromomethylmercurials (which are stable in benzene and toluene at room temperature) indicates that the reaction conditions, not inherent product instability, are responsible for these side-products.

Preparation of phenyl(chloroiodomethyl)mercury

The general procedure outlined above was used in the reaction of 0.15 mole of phenylmercuric chloride with 0.45 mole of chloroiodomethane and 0.45 mole of potassium tert-butoxide in 750 ml of toluene. The crude reaction mixture was filtered from 9 g of dark gray solid, while the combined organic phases produced 48.6 g of yellow oil. Treatment of the latter with 150 ml of benzene, filtration of the resulting solution from 0.9 g of flaky, colorless solid (m.p. 250–265°), and slow addition of 150 ml of *n*-heptane, followed by chilling and concentrating, gave the following crops: 17.0 g of light yellow solid, m.p. 53–55°; 6.4 g of light yellow solid, m.p. 52–54°; 10.0 g of colorless solid, m.p. 115–120°. The crude yield of phenyl(chloroiodomethyl)mercury (the first two crops) amounted to 23.4 g (35 %). The higher melting solid was identified by m.p. and mixed m.p. (recrystallized sample) and IR as diphenylmercury; it was obtained in 35 % yield, based on phenylmercuric chloride. A sample of the crude $C_6H_5HgCHClI$ was recrystallized from a 1:1 (by volume) benzene/heptane mixture to produce light yellow needles, m.p. 55–56°.

Preparation of phenyl(bromoiodomethyl)mercury

In the same manner, a reaction was carried out between 0.1 mole of phenylmercuric chloride, 0.25 mole of bromoiodomethane and 0.25 mole of potassium tert-butoxide in 500 ml of toluene. Following hydrolysis of the reaction mixture and filtration from 3.5 g of gray solid, the work-up proceeded similarly, and evaporation of the organic phases left 39.0 g of an oily, light yellow solid (79 % crude yield). This material was treated with 150 ml of benzene, filtered from 11.4 g of a granular, light green solid, m.p. 86–88°, and following the slow addition of 200 ml of heptane, the following crops were obtained: 14.1 g of a granular, light green solid, m.p. 83–86°; 5.2 g of silky, light yellow-green needles, m.p. 82–84°; 3.9 g of light yellow-green solid, partial melting 76–86°; 2.2 g of oil. The total recrystallized yield (first three crops) was 30.7 g (62 %). A sample of the combined crops, recrystallized from 1:1 benzene/heptane, gave light yellow-green needles, m.p. 85–86°, of phenyl(bromoiodomethyl)mercury.

Preparation of phenyl(diiodomethyl)mercury

A reaction of 0.1 mole of phenylmercuric chloride, 0.4 mole of diiodomethane and 0.2 mole of potassium tert-butoxide was carried out in the usual manner. The dark yellow reaction mixture was hydrolyzed and filtered from 36.8 g of yellow solid, m.p. 85–95°. The aqueous and organic phases were separated and washed with two 100 ml portions of toluene and water, respectively. The combined organic phases were dried, concentrated to 100 ml and filtered from 3.6 g of yellow solid, m.p. 109–111° (dec.). The two crops amounted to 40.4 g (74% crude yield). Complete evaporation of the solution left 9.2 g of solid residue, which melted slowly with decomposition above 200°, and tended to decompose slowly with the formation of a red color on exposure to air. The crude phenyl(diiodomethyl)mercury was treated with one liter of boiling methanol and filtered from 24 g of solid. The solution when chilled yielded 11.4 g of yellow-green, silky needles, m.p. 108–110° (dec.). The filtered solid was treated with one liter of boiling 1:1 hexane/methanol, which when chilled gave 20.4 g of silky needles, m.p. 107–110° (dec.). The total recrystallized yield (including the 3.6 g crop mentioned above) represented a yield of 65%. An analytical sample, obtained by further recrystallization, had m.p. 110–111° (dec.).

Reaction of phenylmercuric bromide with dichloromethane and potassium tert-butoxide

A procedure similar to that used in the preparation of $C_6H_5HgCHBr_2$ described above was used in the reaction of 0.1 mole of phenylmercuric bromide, 0.3 mole of dichloromethane and 0.3 mole of potassium tert-butoxide in 500 ml of toluene. The insoluble material filtered from the hydrolyzed reaction mixture amounted to 18.7 g of colorless solid, m.p. 180–185° (partial). The crude product from the organic phases weighed 13.6 g (38%) and had m.p. 64–67°. A sample recrystallized from a 2:1 hexane/chloroform mixture gave colorless needles, m.p. 70–72°. A sample of the *crude* product was dissolved in benzene, an excess of bromine was added, and the mixture was heated at reflux for 30 min. The solution was cooled, the excess bromine was destroyed by addition of phenol, and the volatile products were analyzed by g.l.c. The gas chromatogram revealed the presence *only* of bromodichloromethane. No dibromochloromethane was present, and thus the crude product contained no phenyl(bromochloromethyl)mercury.

Attempted halomethylenation of cyclohexene with dihalomethane and potassium tert-butoxide

To a slurry of 0.1 mole of potassium tert-butoxide in 450 ml of toluene in a one liter, three-necked Morton flask equipped as described above (including ice bath) was added 82 g of cyclohexene and 0.2 mole of CH_2Cl_2. Following a 3 h period of high-speed stirring at 5°, the mixture was poured into 500 ml of water with stirring. The phases were separated and the organic phase was separated into three fractions by distillation. G.l.c. analysis of all fractions failed to detect even a trace of 7-chloronorcarane. Identical results were obtained with bromochloromethane and dibromomethane, *i.e.*, no 7-chloro- and 7-bromonorcarane, respectively were found.

Preparation of phenyl(chloroiodomethyl)mercury by the sodium iodide procedure

To a solution of 8.1 g (0.02 mole) of phenyl(bromochloromethyl)mercury in 25 ml of dry benzene in a 100 ml, three-necked flask (equipped with mechanical stirrer and under a nitrogen atmosphere) was added a solution of 3.0 g (0.02 mole) of sodium iodide (vacuum-dried at 100°) in 10 ml of methanol over a 5 min period at room temperature. The reaction mixture, which slowly became cloudy and light green in color, was stirred for one h, filtered from 1.0 g of colorless, water-soluble residue and evaporated *in vacuo* to give 9.9 g of a green, oily solid. This was treated with 150 ml of benzene and filtered from 1.1 g of colorless, water-soluble solid. The following crops were obtained from the filtrate by standard recrystallization procedures described above: 5.5 g of light yellow-green needles, m.p. 55–56°; 1.2 g of a similar solid, m.p. 50–52°; a small amount of light green solid, m.p. 45–65°. The recrystallized yield of 6.7 g corresponded to a yield of 74%. The product was identical in all respects with authentic phenyl(chloroiodomethyl)mercury.

Preparation of phenyl(diiodomethyl)mercury by the sodium iodide procedure

In a manner identical to the procedure described in the previous experiment a solution of 0.025 mole of sodium iodide in 10 ml of methanol was added slowly to a solution of 0.01 mole of phenyl(dibromomethyl)mercury in 25 ml of benzene. After 45 min the reaction mixture was filtered from 6.2 g of light-yellow-green solid, melting partially at 105–110°. Evaporation of the filtrate produced 2.0 g of light yellow-green solid, m.p. 100–110° (dec.). Treatment of the combined solids with 300 ml of 1:1 benzene/heptane and filtration left a residue of 2.9 g of colorless, water-soluble solid. Light yellow-green needles (4.2 g) were collected from the filtrate in two crops (m.p. 105–108°, 98–102°, both with dec.), representing a 78% yield. A third crop (0.5 g of light yellow-green solid, m.p. 85–90°) was not investigated further. The product was identical in all respects with an authentic sample of phenyl(diiodomethyl)mercury.

A similar reaction with phenyl(dichloromethyl)mercury gave phenyl(diiodomethyl)mercury in a crude yield of 85% (recrystallized yield, 59%).

Cleavage reactions of phenyl(dihalomethyl)mercury compounds

(*1*) *With hydrogen bromide.* A solution of phenyl(dibromomethyl)mercury (10 g, 0.022 mole) in 50 ml of anhydrous methanol was combined with 100 ml of 0.33 *M* methanolic HBr and refluxed for 30 min. The chilled solution was concentrated to yield a first crop of 8.1 g of white solid, m.p. 161–167° (dec.), and a second crop of 0.6 g, m.p. 157–165° (dec.), for a combined crude yield of dibromomethylmercuric bromide of 8.7 g (86% yield). Recrystallization of the crude product from benzene or toluene did not improve the melting point, but a sample recrystallized from acetone had m.p. 163–166° (dec.). (Found: C, 2.76; H, 0.21; Br, 52.29; $CHBr_3Hg$ calcd.: C, 2.65; H, 0.22; Br, 52.88%.) The infrared spectrum of $CHBr_2HgBr$ (mull composite) showed the following absorptions: 2990 (m), 1135 (w), 1073 (s), 663 (m), 613 (s), cm^{-1}.

A similar reaction in which an excess of HBr was used gave mercuric bromide.

Similar cleavage of $C_6H_5HgCHClBr$ gave a 98% yield of $CHClBrHgBr$, m.p. 170–173° (dec.). (Found: C, 3.15; H, 0.25; Br, 38.90; Cl, 8.54; $CHClBr_2Hg$ calcd.: C, 2.94; H, 0.25; Br, 39.09; Cl, 8.67%.) The infrared spectrum (mull composite) showed absorptions at 2990 (m), 1181 (w), 1086 (s), 730 (sh), 721 (s), 633 (m), cm^{-1}.

Cleavage of phenyl(dichloromethyl)mercury with methanolic HBr gave $CHCl_2HgBr$, m.p. 175–178° (from acetone); lit.[4] m.p. 167–169°. (Found: C, 3.73; H, 0.24; Br, 21.60; Cl, 19.20; Hg, 54.84; $CHCl_2BrHg$ calcd.: C, 3.30; H, 0.28; Br, 21.93; Cl, 19.46; Hg, 55.04%.) The infrared spectrum (mull composite) showed absorptions at 2995 (m), 1213 (w), 1119 (s), 736 (s), 704 (s), cm^{-1}.

(2) *With bromine.* To a solution of 5.0 g (0.011 mole) of phenyl(dibromomethyl)-mercury in 30 ml of benzene was added slowly with stirring a 1:1 bromine/carbon tetrachloride solution until the bromine color no longer was discharged. The colorless precipitate which appeared was filtered to give 4.2 g of solid, m.p. 158–163° (dec.). Evaporation of the solution gave a second crop of 0.8 g of colorless solid, m.p. 157–162° (dec.). This represents a quantitative yield of $CHBr_2HgBr$. Recrystallization from acetone gave material of m.p. 163–166° (dec.), which was identical in all respects with authentic dibromomethylmercuric bromide.

Bromination of $C_6H_5HgCHClBr$ and $C_6H_5HgCHCl_2$ using this procedure gave $CHClBrHgBr$ and $CHCl_2HgBr$, respectively.

Preparation of $C_6H_5HgCH(Cl)SCN$

To a solution of 4.1 g (0.01 mole) of phenyl(bromochloromethyl)mercury in 100 ml of benzene under nitrogen was added slowly with rapid stirring a solution of sodium thiocyanate (0.01 mole, dried *in vacuo* at 100°) in 10 ml of anhydrous methanol. The solution became cream-colored after 30 min and light gray after one h. The reaction was stopped after 2 h and the mixture was filtered from 1.5 g of light gray solid. Treatment of the latter with warm water left 0.5 g of gray residue. The original filtrate was evaporated to give 3.0 g of tan oil, treatment of which with 200 ml of benzene left a residue of 0.3 g of sodium-containing solid. Treatment of the filtrate with decolorizing charcoal followed by fractional crystallization produced two crops of light tan solid: 0.8 g, m.p. 85–87°; 0.4 g, m.p. 71–76°. Recrystallization of the first crop from 1:1 benzene/heptane gave $C_6H_5HgCH(Cl)SCN$, a colorless solid, m.p. 91–92° (dec.). Found: C, 24.77; H, 1.54; Cl, 9.26; N, 3.67; S, 8.06; $C_8H_6ClHgNS$ calcd.: C, 25.00; H, 1.57; Cl, 9.23; N, 3.65; S, 8.35%.) The infrared spectrum (mull composite) showed bands at 3060 (m), 3045 (w), 2980 (w), 2150 (s), 1940 (w), 1865 (w), 1810 (w), 1580 (m), 1485 (s), 1435 (s), 1207 (m), 1075 (w), 1062 (w), 1046 (w), 1025 (m), 996 (m), 915 (w), 861 (w), 723 (s), 711 (w), 699 (s), 665 (w), cm^{-1}.

NMR analysis ($CDCl_3$ solution, TMS internal standard) revealed phenyl (7.3 ppm) and alkyl (5.1 ppm) peaks.

Infrared spectra of phenyl(dihalomethyl)mercury compounds

All spectra are mull composites.

(1) *Phenyl(dichloromethyl)mercury*: 3050 (m), 3035 (w), 2990 (w), 1950 (w), 1875 (w), 1815 (w), 1580 (m), 1480 (s), 1430 (s), 1380 (w), 1340 (m), 1205 (s), 1103 (w), 1077 (m), 1059 (w), 1021 (m), 996 (m), 853 (w), 734 (s), 700 (s), 679 (s), cm^{-1}.

(2) *Phenyl(bromochloromethyl)mercury*: 3050 (m), 3035 (w), 2900 (w), 1950 (w), 1875 (w), 1815 (w), 1580 (m), 1480 (s), 1430 (s), 1380 (w), 1340 (m), 1180 (s), 1153 (m), 1077 (m), 1068 (m), 1059 (w), 1021 (m), 996 (m), 853 (m), 734 (s), 720 (w), 713 (w), 700 (s), 660 (w), 625 (s), 611 (m), cm^{-1}.

(3) *Phenyl(dibromomethyl)mercury*: 3050 (m), 3035 (w), 2995 (m), 1950 (w), 1875 (w), 1815 (w), 1580 (m), 1480 (s), 1430 (s), 1380 (w), 1340 (m), 1135 (s), 1077 (w) 1058 (w), 1021 (m), 996 (m), 853 (w), 734 (s), 700 (s), 593 (m), cm^{-1}

(4) *Phenyl(chloroiodomethyl)mercury*: 3060 (m), 3035 (w), 3015 (w), 3000 (w), 1960 (w), 1880 (w), 1820 (w), 1590 (m), 1480 (s), 1435 (s), 1380 (w), 1340 (w), 1310 (w),

1175 (s), 1158 (m), 1076 (m), 1063 (m), 1021 (m), 1005 (m), 996 (m), 915 (m), 860 (w), 731 (s), 713 (w), 700 (s), 660 (w), 575 (w), cm^{-1}.

(5) *Phenyl(bromoiodomethyl)mercury*: 3060 (m), 3040 (m), 2940 (m), 1960 (w), 1880 (w), 1820 (w), 1590 (m), 1480 (s), 1435 (s), 1380 (w), 1340 (w), 1310 (w), 1120 (s), 1079 (m), 1062 (w), 1021 (m), 996 (m), 914 (w), 848 (w), 729 (s), 700 (s), 662 (w), 638 (m), 568 (w), cm^{-1}.

(6) *Phenyl(diiodomethyl)mercury*: 3060 (sh), 3050 (m), 3040 (sh), 3035 (sh), 2980 (w), 2920 (w), 1960 (w), 1880 (w), 1820 (w), 1590 (m), 1480 (s), 1435 (s), 1380 (w), 1340 (w), 1081 (s), 1075 (sh), 1060 (w), 1021 (m), 1013 (w), 996 (m), 910 (m), 850 (w), 726 (s), 700 (s), 620 (w), cm^{-1}.

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SUMMARY

Phenyl(dibromomethyl)mercury, phenyl(bromochloromethyl)mercury, phenyl(dichloromethyl)mercury, phenyl(bromoiodomethyl)mercury, phenyl(chloroiodomethyl)mercury and phenyl(diiodomethyl)mercury have been prepared by the reaction of phenylmercuric chloride with the appropriate dihalomethane and potassium tert-butoxide in toluene solution. Phenyl(chloroiodomethyl)mercury is more readily accessible by the reaction of phenyl(bromochloromethyl)mercury with one molar equivalent of sodium iodide in methanol/benzene medium. The action of an excess of sodium iodide on $C_6H_5HgCHX_2$ ($X = Cl$ or Br) resulted in formation of phenyl(diiodomethyl)mercury. Methanolic hydrogen bromide and bromine in carbon tetrachloride cleave first a phenyl group from phenyl(dihalomethyl)mercurials, giving CHX_2HgBr compounds, but an excess of these reagents causes complete cleavage of organic groups from mercury. The IR and NMR spectra of these mercurials are presented and their significant features are discussed.

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