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PHENYLMERCURIC ALKOXIDES.
FORMATION OF PHENYL (TRIHALOMETHYL) MERCURY COMPOUNDS.

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The preparation of several phenyl(trihalomethyl) mercury compounds was first reported by Reutov (1) and phenyl-(trichloromethyl) mercury is readily available from several other reactions (2,3,4). The use of the compounds containing bromine in the trihalomethyl group, as dihalocarbene generators was reported by Seyferth and co-workers since 1962 in a number of short communications and recently the same group published detailed method of their preparation (5) and use (6).

In this laboratory it was noticed some time ago that distinct differences exist between the reactivity of $PhHgCCl_3$ and $PhHgCCl_2Br$. This difference lies not only in their reaction rate (7) but also in their absolute reactivity as gem-dichlorocyclopropane cyclising agents with a number of "electrophilic" olefins. As the reported (1,7) method did not yield the bromo containing compounds in experimental quantities the formation of phenyl(trihalomethyl) mercury compounds was examined in detail.

Decarboxylation of sodium bromodichloroacetate,

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dibromochloroacetate and tribromoacetate in an aprotic solvent or the reaction of the esters of these acids in the presence of phenylmercuric salts did not yield the aryl (trihalomethyl) mercurials although analogous reaction using trichloroacetates gives $PhHgCCl_3$ in a high yield (2,3,4).

A possible reaction of diphenyl mercury, which was the main product of the reported preparations (1), with trihalomethanes and potassium *tert*-butoxide was shown not to occur.

$$PhHgPh + HCX_3 + KO\text{-}t\text{-}Bu \nrightarrow PhHgCX_3$$

However, it was noted that addition of potassium *tert*-butoxide under a cover of an inert gas to phenylmercuric salts, in benzene or aprotic diethers, afforded a highly unstable solution of a mercury compound. This solution, either on exposure to atmosphere or on concentration of the solvent, yielded a precipitate of a white phenyl mercury containing solid of a variable composition. Addition of a haloform to the solution under inert gas cover at lower temperatures gave a precipitate from which phenyl(trihalomethyl) mercury compounds could be isolated in pure form. Potassium *tert*-butoxide could be replaced with the more readily available sodium alkoxides without affecting the reaction. Phenylmercuric alkoxides are logical intermediates in the reaction.

$$PhHgY + NaOR \longrightarrow PhHgOR + NaY$$

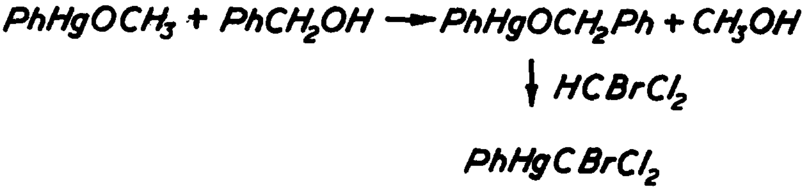
$$PhHgOR + HCX_3 \longrightarrow PhHgCX_3$$

Y = Cl ; Br ; CH_3COO^-

R = CH_3 , C_2H_5 , C_3H_7 , n-C_4H_9 , t-C_4H_9

HCX_3 = $HCCl_3$, $HCBrCl_2$, $HCBr_2Cl$, $HCBr_3$

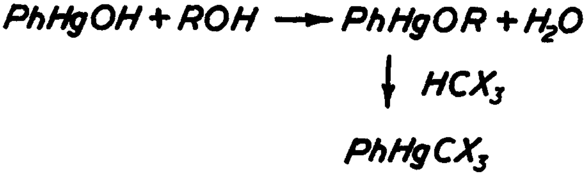
To verify the formation of phenylmercuric alkoxides, an alcohol exchange was carried out on a solution of phenylmercuric methoxide; freed from methanol by a low pressure azeotropic distillation; with benzyl alcohol.



$$PhHgOCH_3 + PhCH_2OH \rightarrow PhHgOCH_2Ph + CH_3OH \xrightarrow{HCBrCl_2} PhHgCBrCl_2$$

After the exchange the methanol formed was again azeotropically distilled and estimated as its 3;5-dinitro benzoate ester.

Direct proof that phenylmercuric alkoxides are intermediates in the formation of phenyl(trihalomethyl)-mercury is provided by the demonstration that such alkoxides, prepared directly from phenylmercuric hydroxide and alcohols, react with haloforms to give the desired products.



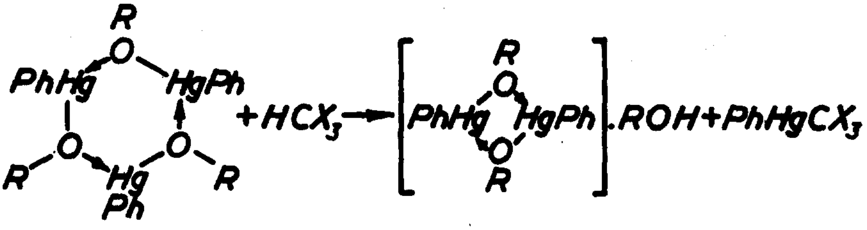
$$PhHgOH + ROH \rightarrow PhHgOR + H_2O \qquad PhHgOR \xrightarrow{HCX_3} PhHgCX_3$$

R = CH_3OH , n-C_4H_9

HCX_3 = $HCCl_3$, $HCBrCl_2$, $HCBr_2Cl$; $HCBr_3$

This reaction constitutes an easy preparation of the phenyl(trihalomethyl)mercury compounds, particularly as phenylmercuric salts prepared by special methods (5) are not necessary.

In repeated experiments it was noted that the yield (on phenylmercuric salt) of the phenyl(trihalomethyl)mercury compounds was close but never exceeded 33% irrespective of the mode of addition, the nature of the haloform or alkoxy residue used. The purity of the phenylmercuric salts was also without effect on the final yield. The observed yield can be explained by the following reaction mechanism :



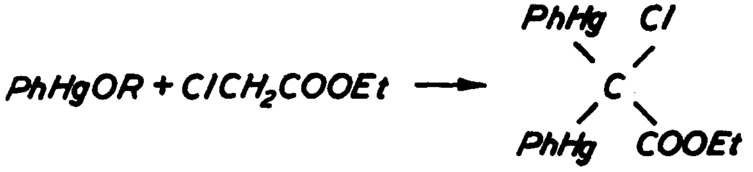
The molecular weight measurements of solutions of phenylmercuric methoxide prepared from phenylmercuric chloride and sodium methoxide and of phenylmercuric n-butoxide prepared from phenylmercuric hydroxide and n-butanol support the assignment of the trimeric structure.

Molecular Weight	Found	Calculated
$(PhHgOCH_3)_3$	898	924
$(PhHgOC_4H_9)_3$	1028	1050

The alcohol solvated phenylmercuric alkoxide dimers which precipitated on the addition of haloforms exhibited a uniform characteristic infra red spectrum and all contained an hydroxyl absorption at 3380 cm^{-1} even when isolated under strictly anhydrous conditions. They could be further reacted with phenyl isocyanate (8) or acetone, when phenylmercurated ketones were formed (i.r. spectrum). The only way to increase the yield of the phenyl(trihalomethyl) mercury compounds over the one third molar proportion mentioned before was to reconvert the solvated dimer to the trimeric form by resuspending it in benzene and treating it with further alcohol and alkali alkoxide, followed by additional haloform. Alternately, additional alcohol and alkali alkoxide could be added at the start of the reaction. In this way yields of up to 70% of the phenyl(trihalomethyl) mercury compounds could be obtained.

This clarifies the report (5) of preparation of the compounds using an excess of K-O *tert*-butoxide solvated with *tert*-butanol.

The proton abstracting ability of the trimeric alkoxides in the absence of other bases was demonstrated by their reaction with active methylene containing compounds. Thus the reaction of phenylmercuric methoxide (from PhHgOH and MeOH) with ethyl chloroacetate yielded ethyl 1,1-bis-(phenylmercuric)-1-chloroacetate (9).



$$PhHgOR + ClCH_2COOEt \longrightarrow (PhHg)_2C(Cl)COOEt$$

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