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HALOMETHYL-METAL COMPOUNDS
XXXVIII[a]. REACTIONS OF PHENYL(TRIHALOMETHYL)MERCURY COMPOUNDS WITH BIS(TRIMETHYLSILYL)- AND BIS(TRIMETHYLGERMYL)MERCURY[b]

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SUMMARY

The reaction of phenyl(bromodichloromethyl)mercury-derived dichlorocarbene with bis(trimethylsilyl)mercury in benzene at 80° gave as principal products trimethyl(trichlorovinyl)silane, trimethylchlorosilane, metallic mercury and phenylmercuric bromide. An analogous reaction with bis(trimethylgermyl)mercury gave trimethyl(trichlorovinyl)germane and trimethylchlorogermane. The same reactions were found to occur between phenyl(dibromochloromethyl)- and phenyl(tribromomethyl)mercury and bis(trimethylsilyl)mercury, but the yields of the (trihalovinyl)-silanes, $Me_3SiCCl{=}CClBr$ and $Me_3SiCBr{=}CBr_2$ respectively, were much lower. Experimental evidence was gathered which indicated that these reactions proceed via dihalocarbene insertion into the Group IV element-to-mercury bond followed by another CX_2 insertion into the newly formed Hg–C bond in the Me_3MCX_2–Hg intermediate and subsequent β-elimination of Hg–X from $Me_3MCX_2CX_2$–Hg species thus formed. Among the evidence presented was the finding that the reaction of $PhHgCCl_2Br$-derived dichlorocarbene with Me_3SiCCl_2–Hg compounds gives $Me_3SiCCl{=}CCl_2$.

INTRODUCTION

In past papers of this series we have described the insertion reactions of phenyl(trihalomethyl)mercury-derived dihalocarbenes into a number of different single bonds. Dihalocarbene insertion into single bonds involving mercury seemed to proceed quite readily. Thus we found that dihalocarbenes undergo insertion into mercury–halogen bonds[3,4] and Landgrebe and Mathis reported that CCl_2 (from CCl_3CO_2Et + base) will insert into alkyl–Hg bonds (eqn. 1)[5]. If a similar insertion

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[a] For Part XXXVII see ref. 1.
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$$\text{R–Hg–R} + \text{CCl}_2 \rightarrow \text{R–Hg–CCl}_2\text{R} \quad (1)$$

into a metal– (or metalloid)–mercury bond could be achieved, then a potentially useful route to metal(loid)-substituted carbenes might be available (eqns. 2, 3). Of special interest to us in view of our studies of Group IV element-substituted carbene

$$\text{R}_n\text{M–Hg–MR}_n + \text{CX}_2 \rightarrow \text{R}_n\text{MCX}_2\text{–Hg–CX}_2\text{MR}_n \quad (2)$$

$$(\text{R}_n\text{MCX}_2)_2\text{Hg} \rightarrow 2\ \text{R}_n\text{M–C–X} + \text{HgX}_2 \quad (3)$$

precursors[1,6,7] was the possibility of dihalocarbene insertion into the element–mercury bonds of bis(trimethylsilyl)mercury[8] and bis(trimethylgermyl)mercury[9] to give products which could be sources of (trimethylsilyl)- and (trimethylgermyl)halocarbenes, respectively. Accordingly, such a study was undertaken to complement our investigation of $(\text{Me}_3\text{SiCX}_2)_2\text{Hg}$ synthesis via active metal reagents[1,7].

RESULTS AND DISCUSSION

When one molar equivalent of bis(trimethylsilyl)mercury in benzene was added under argon to two molar equivalents of phenyl(bromodichloromethyl)mercury in benzene at 65–75° and the mixture was heated at reflux for 70 min, phenylmercuric bromide precipitated, and metallic mercury also was formed. Examination of the filtrate [trap-to-trap distillation; thin-layer chromatography (TLC) of the solid residue and gas-liquid chromatography (GLC) of the volatiles] showed that the processes occurring had led to a number of products. The solids contained at least four different mercury compounds which could not be separated and identified. The volatile products included trimethylchlorosilane, trimethyl(trichlorovinyl)silane and tetrachloroethylene as major components; at least eight minor components were present and among these was trimethyl(bromodichloromethyl)silane. The major process can be summarized by eqn. (4). Based on this equation, the product yields in

$$(\text{Me}_3\text{Si})_2\text{Hg} + 2\ \text{PhHgCCl}_2\text{Br} \rightarrow \text{Me}_3\text{SiCCl=CCl}_2 + \text{Me}_3\text{SiCl} + \text{Hg} + 2\ \text{PhHgBr} \quad (4)$$

one such reaction were: $\text{Me}_3\text{SiCCl=CCl}_2$, 43%, and trimethylchlorosilane, 31%. In another similar reaction in which the trimethyl(trichlorovinyl)silane yield was 41%, it was determined that phenylmercuric bromide had been formed in 96% yield and metallic mercury in 30% yield. In addition, tetrachloroethylene (13%) and trimethyl(bromodichloromethyl)silane (5%) were identified. Lower $\text{Me}_3\text{SiCCl=CCl}_2$ yields resulted when the $\text{PhHgCCl}_2\text{Br}$-to-$(\text{Me}_3\text{Si})_2\text{Hg}$ ratio was lowered to 1, but on increasing this ratio to 4, the $\text{Me}_3\text{SiCCl=CCl}_2$ yield was increased to 60–75%.

A similar reaction carried out between bis(trimethylgermyl)mercury and phenyl(bromodichloromethyl)mercury (1/2.5 molar ratio) gave trimethyl(trichlorovinyl)germane, $\text{Me}_3\text{GeCCl=CCl}_2$, in 63% yield, as well as trimethylchlorogermane (ca. 21%) and tetrachloroethylene (7%).

The possible extension of this new reaction to the preparation of bromodichlorovinyl and tribromovinyl compounds of silicon was investigated. The reaction of phenyl(dibromochloromethyl)mercury with bis(trimethylsilyl)mercury gave variable results. Yields of $\text{Me}_3\text{SiCCl=CClBr}$ as high as 37% were obtained in a 2/1 reaction, but usually they were lower. Invariably, trimethyl(dibromochloromethyl)mercury also was formed. For instance, in a reaction of $\text{PhHgCCl}_2\text{Br}$ with bis(trimethylsilyl)mercury (4/1 molar ratio) in chlorobenzene at 110°, the major products were

$Me_3SiCCl{=}CClBr$ (19%) and $Me_3SiCClBr_2$ (11%). A large number of minor products were formed as well. Trimethyl(tribromovinyl)silane (17%) and trimethyl(tribromomethyl)silane (22%) were produced in the 4/1 reaction of phenyl(tribromomethyl)mercury with $(Me_3Si)_2Hg$.

The reaction of phenyl(trihalomethyl)mercury compounds with $(Me_3M)_2Hg$ compounds thus appears to be a general one in which trihalovinyl compounds of the respective Group IV element are formed. In the case of phenyl(bromodichloromethyl)mercury, the yields of the trichlorovinyl compounds are large enough to make the reaction preparatively useful.

The formation of the observed products could be rationalized [as shown for the reaction of $(Me_3Si)_2Hg$ with $PhHgCCl_2Br$] in terms of the sequence below (eqns. 5–8).

$$Me_3Si{-}Hg{-}SiMe_3 + PhHgCCl_2Br \longrightarrow Me_3SiCCl_2{-}Hg{-}SiMe_3 + PhHgBr \qquad (5)$$

$$Me_3SiCCl_2{-}Hg{-}SiMe_3 + PhHgCCl_2Br \longrightarrow Me_3SiCCl_2CCl_2{-}Hg{-}SiMe_3 + PhHgBr \qquad (6)$$

$$Me_3SiCCl_2CCl_2{-}Hg{-}SiMe_3 \longrightarrow Me_3SiHgCl + Me_3SiCCl{=}CCl_2 \qquad (7)$$

$$Me_3SiHgCl \longrightarrow Me_3SiCl + Hg \qquad (8)$$

The first step in this proposed sequence involves the sought-for reaction, dichlorocarbene insertion into the Hg–Si bond. Once the initial product is present, the dichlorocarbene being generated has the possibility of inserting into a Hg–Si bond or into a newly formed Hg–C bond. The products finally obtained indicate that it is insertion into the Hg–C bond which is favored (eqn. 6). The formation of tetrachloroethylene in moderate amount is understandable, since here also CCl_2 insertion into

$$PhHgCCl_2Br \xrightarrow{CCl_2} PhHgCCl_2CCl_2Br \longrightarrow PhHgBr + Cl_2C{=}CCl_2 \qquad (9)$$

a Hg–C bond is involved (eqn. 9). Formation of $Me_3SiCCl_2CCl_2HgSiMe_2$ would be expected to be followed rapidly by the β-elimination process shown in eqn. (7). It is well known that in organometallic systems β-elimination of metal halide from the $M{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}X$ structure occurs much more readily than α-elimination of metal halide from $M{-}\overset{|}{\underset{|}{C}}{-}X$ (compare, for instance, the thermal stabilities of $Me_3SiCH_2CH_2X$ and Me_3SiCH_2X). The formation of trimethylchlorosilane and metallic mercury then would require the thermal instability of trimethylsilylmercuric chloride as shown in eqn. (8).

The formation of the observed trimethyl(trihalomethyl)silanes could have occurred in a competing process which does not involve dihalocarbenes (eqns. 10 and 11).

$$(Me_3Si)_2Hg + PhHgCCl_2Br \longrightarrow Me_3SiHgCCl_2Br + PhHgSiMe_3 \qquad (10)$$

$$Me_3SiHgCCl_2Br \longrightarrow Me_3SiCCl_2Br + Hg \qquad (11)$$

All the reactions suggested above are reasonable in the context of known dihalocarbene and organomercury chemistry, but it was desirable to obtain experimental support for the proposed reaction scheme. Further work provided such support for most of the suggested steps.

The instability of trimethylsilylmercuric chloride was quickly confirmed. A reaction which should have given this compound, that of bis(trimethylsilyl)mercury and mercuric chloride at room temperature, proceeded exothermally to give trimethylchlorosilane (95%) and metallic mercury (88%) instead. Lee[10] later provided further support, finding that Me_3SiHgX systems generally are unstable.

Considerable attention was devoted to the processes indicated by eqns. (6) and (7). First, direct evidence was sought for the intermediacy of Me_3SiCCl_2Hg compounds. The $PhHgCCl_2Br/(Me_3Si)_2Hg$ reaction (2/1 ratio) was allowed to proceed at room temperature for three days. At the end of this time the solution was filtered to remove crude phenylmercuric bromide in 62% yield. The filtrate was treated with bromine, the resulting mercuric bromide was filtered off and the volatile components were determined by GLC. The following were present: Me_3SiCl (5%), C_2Cl_4, CCl_2Br_2 (30%), Me_3SiCCl_2Br [30%, based on 1 $(Me_3Si)_2Hg \rightarrow 2\ Me_3SiCCl_2Br$], $Me_3SiCCl{=}CCl_2$ (8%), C_6H_5Br (31%) and Me_3SiBr. Brominolysis serves readily in the analysis of organomercury compounds (*e.g.*, ref. 11), and finding trimethyl(bromodichloromethyl)silane in 30% yield could indicate the presence of Me_3SiCCl_2- substituted mercury compounds in the reaction mixture. Such an explanation for the presence of Me_3SiCCl_2Br is not the only one; this compound could have resulted from the reaction sequence (10)–(11) and its high yield possibly could be attributed to a decrease in the rate of the competing carbene process when the temperature was lowered to ca 25°. This, however, was not the case. A 2/1 $PhHgCCl_2Br/(Me_3Si)_2Hg$ reaction carried out for three days at room temperature which was *not* followed by a bromination step gave trimethyl(bromodichloromethyl)silane in only trace yield. Therefore, it is very likely that the high yield of Me_3SiCCl_2Br in the first room temperature experiment is indicative of the formation of Me_3SiCCl_2Hg compounds. Furthermore, in the second room temperature experiment IR spectroscopic investigation of the benzene-soluble solids suggested the presence of such mercurials.

It may be noted that the mercury and trimethylsilyl group balances in the reactions carried out above room temperature were not especially good. The balance unaccounted for could well be present (in the case of $PhHgCCl_2Br$ reactions) as $(Me_3SiCCl_2)_2Hg$, Me_3SiCCl_2HgCl and trichloromethyl–mercury compounds. Resolution of such mixtures would be quite difficult. A more complete listing of possible reactions follows below. These are based on the assumption of the initial formation of $Me_3SiCCl_2HgSiMe_3$. Compounds marked with an asterisk are those we know to be quite stable thermally at 80° for at least 5–6 hours. These do not include all possibilities, but they do serve to indicate that stable organomercury compounds can accumulate in these reaction systems.

$$Me_3SiCCl_2HgSiMe_3 + PhHgCCl_2Br \rightarrow (Me_3SiCCl_2)_2Hg^* + PhHgBr \quad (12)$$

$$(Me_3SiCCl_2)_2Hg + PhHgCCl_2Br \rightarrow Me_3SiCCl_2CCl_2HgCCl_2SiMe_3 + PhHgBr \quad (13)$$

$$Me_3SiCCl_2CCl_2HgCCl_2SiMe_3 \rightarrow Me_3SiCCl_2HgCl^* + Me_3SiCCl{=}CCl_2 \quad (14)$$

$$Me_3SiCCl_2HgCl + PhHgCCl_2Br \rightarrow Me_3SiCCl_2HgCCl_3 + PhHgBr \quad (15)$$

$$Me_3SiCCl_2HgCCl_3 + PhHgCCl_2Br \rightarrow Me_3SiCCl_2CCl_2HgCCl_3 + PhHgBr \quad (16)$$

$$Me_3SiCCl_2CCl_2HgCCl_3 \rightarrow CCl_3HgCl^* + Me_3SiCCl{=}CCl_2 \quad (17)$$

$$CCl_3HgCl + PhHgCCl_2Br \rightarrow (CCl_3)_2Hg^* + PhHgBr \quad (18)$$

While this study was in progress we succeeded in preparing $(Me_3SiCCl_2)_2Hg$, Me_3SiCCl_2HgBr and Me_3SiCCl_2HgCl by the organolithium route[1]. Their availability made possible a more direct investigation of our suggestion that CCl_2 insertion into the Me_3SiCCl_2–Hg bond should occur quite readily. Of importance to this study was the observation that $(Me_3SiCCl_2)_2Hg$ and Me_3SiCCl_2HgX compounds are quite stable in benzene at 80° (ref. 7). Our studies showed that they do indeed react with phenyl(bromodichloromethyl)mercury in benzene at 80°. When a benzene solution of $(Me_3SiCCl_2)_2Hg$ and 2 molar equivalents of $PhHgCCl_2Br$ was stirred at reflux for 5 h, phenylmercuric bromide (90%) precipitated. The volatile products formed included the expected trimethyl(trichlorovinyl)silane (32%), as well as tetrachloroethylene (14%) and trimethyl(bromodichloromethyl)silane (5%). A nonvolatile solid residue was obtained from the benzene solution which TLC showed to contain at least five organomercury compounds. In another reaction, an equimolar mixture of diphenylmercury and $(Me_3SiCCl_2)_2Hg$ was heated with 3 molar equivalents of phenyl(bromodichloromethyl)mercury in benzene at reflux for 6 h. The volatile products were $Me_3SiCCl{=}CCl_2$ (38%), tetrachloroethylene (5%) and Me_3SiCCl_2Br (5%). The benzene-soluble solid residue was treated with an excess of bromine and subsequent work-up showed the presence of large amounts of bromobenzene and Me_3SiCCl_2Br, as well as of a small amount of bromotrichloromethane. The presence of the latter is indicative of CCl_3–Hg compounds, formed perhaps by reactions (15), (17) and (18).

A similar reaction was observed when a mixture of Me_3SiCCl_2HgBr and 2 molar equivalents of phenyl(bromodichloromethyl)mercury was heated at reflux in benzene for 4 h. The products were phenylmercuric bromide (96%), $Me_3SiCCl{=}CCl_2$ (82% based on Me_3SiCCl_2HgBr), tetrachloroethylene (11% based on $PhHgCCl_2Br$) and Me_3SiCCl_2Br (11% based on Me_3SiCCl_2HgBr). The higher yield of the (trichlorovinyl)silane no doubt is due to two factors: (1) the higher ratio of $PhHgCCl_2Br$ to Me_3SiCCl_2–Hg linkage used and (2) the use of trimethylsilyldichloromethylmercuric *bromide*, dichlorocarbene insertion into whose Hg–Br bond should be a reversible process, thus making the stoichiometry even more favorable.

From the results of this study it is now quite clear that dichlorocarbene does insert into the Hg–Si bond (and into the Hg–Ge bond). However, all available evidence indicates that at 80° the Me_3SiCCl_2–Hg (and Me_3GeCCl_2–Hg) compounds formed undergo further insertion of dichlorocarbene into the newly formed Hg–C bonds and that the products finally isolated derive from the thermolysis of the resulting $Me_3SiCCl_2CCl_2$–Hg compound as shown in eqns. (7) and (8). At room temperature compounds containing the Me_3SiCCl_2–Hg bond do appear to accumulate, but complex mixtures of organomercurials are present. Thus such insertion reactions have no practical utility in the preparation of the desired Me_3SiCCl_2–mercurials and the organolithium route[1] is the method of choice. In the case of the $PhHgCBr_3/(Me_3Si)_2Hg$ reaction the yields of volatile products are considerably lower and solids containing the Me_3SiCBr_2–Hg bond were present when the reaction was carried out at 80°. This, we suggest, probably is due to the steric hindrance associated with CBr_2 insertion into the Me_3SiCBr_2–Hg linkage. It is of interest that reaction of dihalocarbenes at the tin–tin bond of hexamethylditin gives insertion products, $Me_3SnCX_2SnMe_3$, which are quite stable thermally and toward further attack by dihalocarbene[12].

Finally, we must take note of the reactions (eqns. 10 and 11) believed to be responsible for the formation of Me_3SiCX_3 compounds in the $(Me_3Si)_2Hg/PhHgCX_3$ reactions. This suggested to us that the reaction of bis(trimethylsilyl)mercury with organomercury compounds (R_2Hg and RHgX, where R is rather electronegative should be a source of Me_3SiR compounds. This was found to be the case and the following equations summarize the reactions studied.

$$(Me_3Si)_2Hg + C_6Cl_5HgCl \xrightarrow[\text{reflux}]{\text{Toluene}} \underset{(40\%)}{Me_3SiC_6Cl_5} + Me_3SiCl + Hg \quad (19)$$

$$(Me_3Si)_2Hg + C_6F_5HgBr \xrightarrow[\text{reflux}]{\text{Toluene}} \underset{(41\%)}{Me_3SiC_6F_5} + Me_3SiBr + Hg \quad (20)$$

$$(Me_3Si)_2Hg + Hg(CCl{=}CCl_2)_2 \xrightarrow[\text{reflux}]{\text{Toluene}} \underset{(11\%)}{Me_3SiCCl{=}CCl_2} + Me_3SiCl + Hg \quad (21)$$

In the last reaction the equation indicated represents only a minor process. The major reaction involved formation of trimethylchlorosilane in large quantity. During the course of this work other examples of such reactions were reported by Vyazankin and his coworkers (eqns. 22 and 23)[13,14].

$$R_2Hg + (R'_3M)_2Hg \rightarrow 2\,R'_3MR + Hg \quad (22)$$

$$(R = C_6F_5,\ CH_2CO_2Et,\ CH_2COEt;\ R' = Et,\ Ph;\ M = Si,\ Ge)$$

$$(Et_3Ge)_2Hg + ClHgCH_2CO_2Me \rightarrow Et_3GeCH_2CO_2Me + Et_3GeCl + 2\,Hg \quad (23)$$

EXPERIMENTAL

General comments

All reactions were carried out under an atmosphere of dry argon or nitrogen in flame-dried glassware. Infrared spectra were recorded using a Perkin Elmer Model 337 or 237B grating infrared spectrophotometer, NMR spectra using either a Varian Associates A60 or T60 NMR spectrometer. Chemical shifts are expressed in δ units, ppm downfield from TMS. Gas–liquid chromatography (GLC) was used for separation and purification of products and for yield determinations. The instruments used included the MIT isothermal unit and F&M Model 700, 720 and 5754 gas chromatographs. The internal standard method was employed in yield determinations.

The phenyl(trihalomethyl)mercury compounds used were prepared using our recently described procedure[15], bis(trimethylsilyl)mercury and bis(trimethylgermyl)-mercury by the sodium amalgam method[8,9].

All reactions were carried out in three-necked flasks of appropriate size equipped with a reflux condenser topped with a gas inlet tube, a pressure-equalizing dropping funnel and a magnetic stirring assembly. An oil bath was used for external heating.

Reaction of phenyl(bromodichloromethyl)mercury with bis(trimethylsilyl)mercury

To a solution of 10.92 g (24.9 mmole) of $PhHgCCl_2Br$ in 15 ml of benzene at

65–75° was added slowly with stirring 4.32 g (12.45 mmole) of $(Me_3Si)_2Hg$ in 25 ml of benzene. After completion of the addition (30 min), the mixture was heated at reflux for 70 min. The characteristic yellow color of the silylmercurial was discharged immediately upon its addition to the $PhHgCCl_2Br$ solution. The reaction mixture was allowed to cool to room temperature and then was filtered. The gray solid which had formed during the reaction was not examined in this case. The filtrate was trap-to-trap distilled at 0.1 mm (pot temperature to 70°) into a receiver cooled to $-78°$. The colorless distillate fumed in air. It was analyzed by GLC (15% General Electric Co. SE-30 silicone rubber gum on Chromosorb W, F&M 720, 40–200° temperature program). The major product was $Me_3SiCCl{=}CCl_2$, n_D^{25} 1.4869 (lit.[16] n_D^{20} 1.4890), in 43% yield. (Found: C, 29.62; H, 4.56. $C_5H_9Cl_3Si$ calcd.: C, 29.48; H, 4.42%.) IR (liq. film): 2955 s; 2895 m, 1950 w, 1875 w, 1540 s [ν(OC=C)], 1455 w, 1410 m, 1315 w, 1270 m, 1255 s (Me_3Si), 965 s, 870 s, 840 s, 830 sh, 760 m and 720 m cm^{-1}. Trimethylchlorosilane and tetrachloroethylene also were present (IR spectral identification); the yield of the former was 31%.

In a similar reaction, carried out between 5.4 mmole of $(Me_3Si)_2Hg$ and 22.7 mmole of $PhHgCCl_2Br$ at 80° the reaction solids were filtered and extracted with hot dimethylformamide to leave 0.33 g (30%) of metallic mercury. The original reaction solids, m.p. 280–284°, had weighed 8.08 g, hence the phenylmercuric bromide yield was ca. 7.75 g (96%). The filtrate from the reaction mixture was trap-to-trap distilled. TLC examination[11] of the residue (white solid and brown oil) indicated the presence of at least four organomercury compounds. GLC analysis of the distillate (10% Dow Corning DC 200 silicone oil, F&M 5754, 60–190° temperature program, 1-chloronaphthalene internal standard) showed the following to be present: trimethylchlorosilane, tetrachloroethylene (13%), trimethyl(bromodichloromethyl)silane (5%) (identified by comparison of its GLC retention time and infrared spectrum with those of an authentic sample[1]) and $Me_3SiCCl{=}CCl_2$ (41%).

Using a 4/1 molar ratio of $PhHgCCl_2Br$ to $(Me_3Si)_2Hg$ usually raised the $Me_3SiCCl{=}CCl_2$ and Me_3SiCl yields to around 60%.

Reaction of phenyl(bromodichloromethyl)mercury with bis(trimethylgermyl)mercury

A similar procedure was followed in the reaction of 10.1 g (22.9 mmole) of $PhHgCCl_2Br$ and 4.0 g (9.2 mmole) of $(Me_3Ge)_2Hg$ in 70 ml of dry benzene. The reaction mixture was heated and stirred at reflux for 1 h, during which time the color darkened and a gray solid settled out. Filtration was followed by trap-to-trap distillation of the filtrate. GLC examination of the distillate (15% SE-30 on Chromosorb G, F&M 720, 60–270° temperature program) showed trimethylchlorogermane (ca. 21%), tetrachloroethylene (7%) and another compound identified as trimethyl(trichlorovinyl)germane to be present. The yield of the latter was 42%. It was isolated by preparative GLC as a liquid, n_D^{25} 1.5330. (Found: C, 24.67; H, 3.90; Cl, 42.33. $C_5H_9Cl_3Ge$ calcd.: C, 24.21; H, 3.66; Cl, 42.88%.) IR 2990 m, 2920 m, 2815 w, 1860 w, 1820 w, 1555 s [ν(C=C)], 1420 m, 1255 sh, 1245 s, 1020 w, 955 s, 850 s, 840 sh, 770 m and 715 m cm^{-1}.

The solid residue from the initial filtration and the trap-to-trap distillation was washed with benzene and the insoluble residue was Soxhlet-extracted with benzene to give 6.5 g (80%) of phenylmercuric bromide, m.p. 280–282°. Mercury metal (1.0 g) remained in the extraction thimble.

Reaction of phenyl(dibromochloromethyl)mercury with bis(trimethylsilyl)mercury

To a bright yellow solution of 4.33 mmole of $(Me_3Si)_2Hg$ in 15 ml of dry chlorobenzene which was heated with an oil bath maintained at 110° was added during 15 min with stirring 8.41 g (17.4 mmole) of $PhHgCClBr_2$ in 35 ml of chlorobenzene. A yellow-red reaction mixture containing white solid resulted. The reaction mixture was heated for 4 h (bath at 110°) and another 4 h with the oil bath at 135°. TLC investigation of the brown reaction mixture showed the presence of at least three different organomercurials. Filtration was followed by trap-to-trap distillation of the filtrate. GLC analysis (10% UC-W98, F&M 5754, 50–180° temperature program, 1-chloronaphthalene internal standard) of the distillate showed the presence of the following compounds: trimethylbromosilane, $Me_3SiCClBr_2$ [11%, based on $1\ (Me_3Si)_2Hg \rightarrow 1\ Me_3SiCClBr_2$], $Me_3SiCCl{=}CClBr$ [19%, based on $1\ (Me_3Si)_2Hg \rightarrow 1\ Me_3SiCCl{=}CClBr$], as well as several minor products.

Trimethyl(dibromochloromethyl)silane is a volatile solid, m.p. 175–177°, which was collected by GLC. (Found: C, 17.09; H, 3.23. $C_4H_9Br_2ClSi$ calcd.: C, 17.13; H, 3.23%.) The mass spectrum (Hitachi–Perkin Elmer RMU6D mass spectrometer, 80 eV) showed the molecular ion peaks at m/e 278, 280, 282 and 284 in a ratio of ca. 3/7/5/1, indicating the presence of 2 Br atoms and one Cl. IR (CCl_4/CS_2 composite): 2982 sh, 2968 s, 2910 m, 1880 w, 1414 m, 1330 w, 1265 sh, 1253 s, 875 s, 848 s, 800 m, 762 w, 712 s, 682 m, 671 sh, and 635 m cm^{-1}.

Trimethyl(bromodichlorovinyl)silane was isolated by GLC as a liquid, n_D^{25} 1.5093. The $Me_3SiCCl{=}CClBr$ structure follows from the mechanism of its formation, eqns. (24)–(25). Here we assume that as in the case of α-elimination from $PhHgCCl_nBr_{3-n}$ compounds[17], elimination of RHgBr will be highly favored over elimination of RHgCl. The NMR spectrum (in $CHCl_3$) suggested the presence of two isomers: the Me_3Si resonance was not one but two singlets, centered at 0.33 ppm and separated by 1.3 Hz as shown by a scan at sweepwidth of 100 Hz. (Found: C, 24.25; H, 3.64; Br, 32.04; Cl, 28.41. $C_5H_9BrCl_2Si$ calcd.: C, 24.21; H, 3.66; Br, 32.22; Cl, 28.59%.) IR (liquid film): 2990 sh, 2980 sh, 2963 m, 2903 w, 1532 s [ν(C=C)], 1410 w, 1269 sh, 1258 s, (Me_3Si), 952 sh, 943 s, 848 s, 825 sh, 815 s, 763 m, 702 m, 685 sh, 625 w, and 615 w cm^{-1}.

$$Me_3SiCClBr{-}HgSiMe_3 + PhHgCClBr_2 \rightarrow Me_3SiCClBrCClBr{-}HgSiMe_3 + PhHgBr \quad (24)$$

$$Me_3SiCClBrCClBr{-}HgSiMe_3 \rightarrow Me_3SiBr + Me_3SiCCl{=}CClBr \quad (25)$$

In a reaction carried out in refluxing benzene for 6 h between 4.95 mmole of $(Me_3Si)_2Hg$ and 10.5 mmole of $PhHgCClBr_2$ the yields of $Me_3SiCClBr_2$ and $Me_3SiCCl{=}CClBr$ were 6% and 11%, respectively.

Reaction of phenyl(tribromomethyl)mercury with bis(trimethylsilyl)mercury

To a solution of 4.75 mmole of $(Me_3Si)_2Hg$ in benzene heated in a 65° oil bath was added over 20 min a solution of 10.05 g (19.05 mmole) of $PhHgCBr_3$ in 50 ml of benzene. The temperature was raised to the reflux point and the reaction mixture was heated at reflux for 18 h. The resulting red-brown reaction mixture was filtered to give 6.46 g of solid residue, mostly PhHgBr according to its m.p. of 280–284°. The filtrate was trap-to-trap distilled at 0.005 mm. GLC analysis of the distillate (10% DC-200, F&M 5754, 60–180° temperature program, 1-chloronaphthalene internal standard) showed the presence of more than 14 components. The major products were: Me_3SiBr, Me_3SiCBr_3 (22%, based on 1 $(Me_3Si)_2Hg \rightarrow 1\ Me_3SiCBr_3$) and $Me_3SiCBr{=}CBr_2$ (17%). Trimethyl(tribromomethyl)silane was identified by comparison of its GLC retention time and infrared spectrum with those of an authentic sample[18]. *Trimethyl(tribromovinyl)silane* is a liquid, n_D^{25} 1.5602. (Found: C, 17.85; H, 2.64; Br, 71.28. $C_5H_9Br_3Si$ calcd.: C, 17.82; H, 2.69; Br, 71.15%.) IR (liquid film): 2983 sh, 2968 m, 2908 m, 1533 s [ν(C=C)], 1460 w· 1408 m, 1335 w, 1295 sh, 1258 s (Me_3Si), 893 s, 848 s, 835 sh, 763 s, 745 sh, 738 m, 698 m, 639 m, 628 sh, and 600 w cm^{-1}.

It was suspected that the 3.55 g brown solid residue from the trap-to-trap distillation contained some compounds with the Me_3SiCBr_2–Hg linkage. Accordingly, this solid together with 15 ml of diphenylmethane was heated for 2 h at 200–210°. GLC analysis of the volatile products showed that over 20 components were present. The major product was trimethyl(dibromomethyl)silane (identified by comparison of its GLC retention time and infrared spectrum with those of an authentic sample). The most likely source of this product is the reaction sequence shown in eqn. (26)[7].

$$Me_3SiCBr_2{-}Hg{-} \longrightarrow {-}Hg^{\bullet} + Me_3SiCBr_2^{\bullet} \xrightarrow{Ph_2CH_2} Me_3SiCBr_2H \qquad (26)$$

Reaction of bis(trimethylsilyl)mercury with mercuric chloride

To a solution of 1.5 g (4.2 mmole) of $(Me_3Si)_2Hg$ in 25 ml of dry benzene was added (under nitrogen) 1.15 g (4.2 mmole) of mercuric chloride at room temperature. An immediate exothermic reaction resulted in the precipitation of metallic mercury. Trap-to-trap distillation of the volatiles and GLC examination of the distillate showed that trimethylchlorosilane had been formed in 95% yield. The residue consisted of metallic mercury (1.5 g, 88%).

Room temperature reaction of bis(trimethylsilyl)mercury with phenyl(bromodichloromethyl)mercury followed by brominolysis

A mixture of 6.8 mmole of $(Me_3Si)_2Hg$ and 13.6 mmol of $PhHgCCl_2Br$ in 30 ml of dry benzene was stirred at room temperature for 3 days. (The reaction apparatus was wrapped in aluminum foil to prevent degradation of $(Me_3Si)_2Hg$ by light during the extended reaction time.) The reaction mixture was filtered under argon into another standard reaction apparatus. The residue (3.01 g) had a melting range of 276–282°. To the filtrate was added 15.6 ml of 1 *M* bromine in carbon tetrachloride during 60 min. The resulting mixture was stirred at room temperature for 2 h. Filtration left 2.85 g of solid, sublimation of which at 140° (0.1 mm) gave 2.76 g (7.4 mmol) of mercuric bromide, m.p. 236–238°. GLC analysis of the trap-to-trap distilled filtrate (7.5% SE-30, F&M 720, 40–165° temperature program, benzotrichloride internal standard) showed the following were present, in addition to other minor components: Me_3SiCl, C_2Cl_4, CBr_2Cl_2 (30%), PhBr (31%), Me_3SiBr, $Me_3SiCCl{=}CCl_2$ (8%), Me_3SiCCl_2Br (30%, based on available Me_3Si groups). Identifications were made on the basis of GLC retention times and infrared spectra.

Reaction of phenyl(bromodichloromethyl)mercury with bis(trimethylsilyldichloromethyl)mercury

A mixture of 2.49 g (4.9 mmole) of $(Me_3SiCCl_2)_2Hg$[1] and 4.44 g (10.1 mmole) of $PhHgCCl_2Br$ in 15 ml of benzene was stirred at reflux for 5 h. Filtration gave 3.2 g (91 %) of impure phenylmercuric bromide, m.p. 272–276°. Trap-to-trap distillation of the filtrate left a solid residue (2.25 g) which TLC showed to contain at least 5 different organomercury compounds. GLC analysis of the distillate showed the presence of the following compounds: C_2Cl_4 (14 %), $Me_3SiCCl{=}CCl_2$ (32 %, based on available Me_3SiCCl_2 groups) and Me_3SiCCl_2Br (5 %).

Reaction of phenyl(bromodichloromethyl)mercury with bis(trimethylsilyldichloromethyl)mercury/diphenylmercury

A similar reaction was carried out for 6 h between 14.1 mmole of $PhHgCCl_2Br$, 4.4 mmole of $(Me_3SiCCl_2)_2Hg$ and 4.62 mmole of diphenylmercury in refluxing benzene. Filtration was followed by trap-to-trap distillation of the filtrate and GLC analysis of the distillate. The following were present: C_2Cl_4 (5 %), $Me_3SiCCl{=}CCl_2$ (38 %) and Me_3SiCCl_2Br (5 %). The solid residue from the trap-to-trap distillation (3.27 g) was treated with bromine in carbon tetrachloride and the reaction products were determined by GLC. Present as major products were bromobenzene and Me_3SiCCl_2Br (23%). Minor products included bromotrichloromethane (identified by GLC retention time and IR spectrum) and two others which were not identified.

Reaction of phenyl(bromodichloromethyl)mercury with trimethylsilyldichloromethylmercuric bromide

A similar reaction was carried out between 5 mmole of $PhHgCCl_2Br$ and 1.09 g (2.5 mmole) of Me_3SiCCl_2HgBr in 45 ml of benzene for 4 h at reflux. The phenylmercuric bromide yield was 96 % (m.p. 274–282°). The usual work-up showed that trimethyl(trichlorovinyl)silane and trimethyl(bromodichloromethyl)silane had been formed in yields of 82 % and 11 %, respectively. Tetrachloroethylene also was present in 11 % yield.

Reaction of (pentachlorophenyl)mercuric chloride with bis(trimethylsilyl)mercury

To a solution of 3.45 g (7.1 mmole) of C_6Cl_5HgCl in 30 ml of toluene was added dropwise a solution of 2.45 g (7.06 mmole) of bis(trimethylsilyl)mercury in 20 ml of toluene. Addition of the first few drops of the yellow solution of the latter caused the reaction mixture to turn gray. The reaction mixture was heated at reflux for 7 days; TLC was used to monitor the progress of the reaction. Filtration then gave metallic mercury in 95 % yield. GLC analysis of the trap-to-trap distilled filtrate (10 % UC-W98, F&M 5754, 60–190° program, n-decane internal standard) showed the following to be present: trimethylchlorosilane (56 %), pentachlorobenzene (25 %), $Me_3SiC_6Cl_5$ (40 %) and several minor products.

Trimethyl(pentachlorophenyl)silane was isolated as a white solid, m.p. 116–117° (lit.[19] m.p. 116.5–117.5°), by preparative GLC. Its infrared spectrum was in agreement with that reported[19]. Pentachlorobenzene was isolated as a white solid, m.p. 82–84° (lit.[19] m.p. 87.8–88.6°) by GLC. The lowered m.p. and a few extra bands in its infrared spectrum indicated that our product was contaminated slightly with an impurity, probably trimethyl(pentachlorophenyl)silane since a weak band at 1253 cm^{-1} was present.

Reaction of (pentafluorophenyl)mercuric bromide with bis(trimethylsilyl)mercury

A similar reaction was carried out with 2.39 g (5.3 mmole) of C_6F_5HgBr and 4.2 mmole of $(Me_3Si)_2Hg$ in 45 ml of toluene at reflux for 7 days. The yield of metallic mercury was 82%. The volatile products included trimethylbromosilane and trimethyl(pentafluorophenyl)silane (41%), n_D^{25} 1.4291 (lit.[20] n_D^{25} 1.4307), with infrared spectrum in agreement with that reported by other workers[21].

Reaction of bis(trichlorovinyl)mercury with bis(trimethylsilyl)mercury

To a solution of 2.90 g (6.3 mmole) of $(CCl_2{=}CCl)_2Hg$[22] in 20 ml of toluene was added 1.84 g (5.3 mmole) of $(Me_3Si)_2Hg$ in 15 ml of toluene. The resulting pale gray mixture was heated at reflux for 18 h to give a black solution. Filtration gave metallic mercury in 86% yield. Trap-to-trap distillation of the filtrate at 0.001 mm left 0.99 g of dark solid which TLC showed to contain three mercury compounds. GLC analysis of the distillate showed the presence of Me_3SiCl (78%) and $Me_3SiCCl{=}CCl_2$ (11%), as well as several other minor components.

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