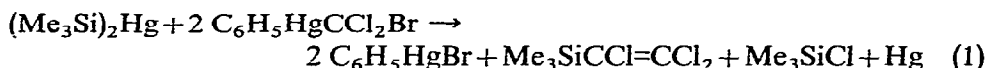


CX₂ insertion into the silicon-mercury and germanium-mercury bonds

The insertion of CCl₂ (generated *via* CCl₃CO₂Et + base) into the C-Hg bonds of dialkylmercury compounds, which gives products of type RCCl₂HgR, has been reported by Landgrebe and Mathis¹, and in these Laboratories we found that CCl₂ (generated *via* phenyl(bromodichloromethyl)mercury) will insert into mercury-halogen linkages to give Hg-CCl₂X compounds². In an attempt to extend such insertion reactions, we have studied the action of phenyl(bromodichloromethyl)mercury on bis(trimethylsilyl)mercury and bis(trimethylgermyl)mercury. We present our initial findings at this time since we have found such reactions to be of synthetic utility: they provide a novel and quite possibly a general route to trihalovinyl-metal compounds.

When to a solution of 24.9 mmoles of C₆H₅HgCCl₂Br³ in 15 ml of benzene under argon at 65–75° was added 12.45 mmoles of bis(trimethylsilyl)mercury⁴ in 25 ml of benzene (with stirring), phenylmercuric bromide and metallic mercury began to precipitate. The reaction mixture was heated at reflux for 70 min. Filtration, followed by gas liquid partition chromatographic (GLPC) analysis* of the filtrate showed the presence of three major and about eight minor components. The former were trimethyl(trichlorovinyl)silane, (CH₃)₃SiCCl=CCl₂** , trimethylchlorosilane and tetrachloroethylene. The yields of the first two products, based on the reaction shown in eqn. 1, were 43% and 31%. A reaction in which the C₆H₅CCl₂Br/(Me₃Si)₂Hg



ratio was 4 gave the trichlorovinylsilane in 58% yield; when this ratio was decreased to 1, the trichlorovinylsilane yield fell to 22%. In the 2/1 reaction the mercury yield, based on eqn. 1, was 56%; the phenylmercuric bromide yield, based on the C₆H₅-HgCCl₂Br used, was 80%.

A reaction carried out in similar fashion with bis(trimethylgermyl)mercury⁶ (9.2 mmoles) and phenyl(bromodichloromethyl)mercury (22.9 mmoles) in 70 ml of benzene resulted in formation of trimethylchlorogermane and trimethyl(trichlorovinyl)germane, (CH₃)₃GeCCl=CCl₂***, the latter in 63% yield, based on the germanium counterpart of eqn. 1. A small amount of tetrachloroethylene (~7%) and several other minor products also were present. The solid reaction products were worked up to give phenylmercuric bromide (80%) and metallic mercury (54%). Treatment of bis(trimethylsilyl)mercury with phenyl(dibromochloromethyl)mercury³ (a CClBr source) in 1:2 ratio in refluxing benzene produced a silane believed to be (CH₃)₃SiCCl=CClBr**** in 37% yield. Reactions with (Et₃Si)₂Hg⁷ and (n-Bu₃Ge)₂Hg also gave trichlorovinyl derivatives of the respective elements.

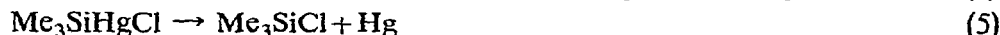
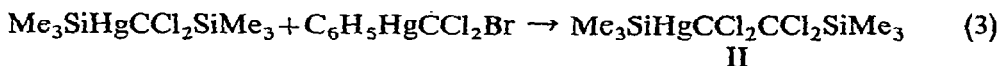
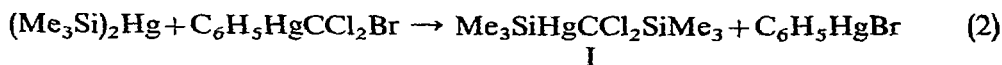
A reasonable mechanism for the formation of the main products observed is given in eqns 2–5.

* F & M Model 720 or 700 gas chromatograph, 15% General Electric SE-30 on Chromosorb W, 40–200° at 10°/min, 48 psi helium.

** n_D^{25} 1.4869, $\nu_{\text{C}=\text{C}}$ 1540 cm⁻¹; lit.⁵ n_D^{25} 1.4890, $\nu_{\text{C}=\text{C}}$ 1541 cm⁻¹; analysis (C, H and Cl) satisfactory.

*** n_D^{25} 1.5330, $\nu_{\text{C}=\text{C}}$ 1555 cm⁻¹; C, H and Cl analyses satisfactory.

**** $\nu_{\text{C}=\text{C}}$ 1530 cm⁻¹; Me₃Si bands at 1255, 840 and 760 cm⁻¹. Analysis satisfactory. The alternate structure, (CH₃)₃SiCBr=CCl₂, is not excluded, but is considered less likely in terms of the mechanism proposed.



Reaction (2) involves CCl_2 insertion into the Si-Hg bond in a manner similar to CCl_2 insertion into the C-Hg bond¹. It is not yet clear whether this is a process in which decomposition of $\text{C}_6\text{H}_5\text{HgCCl}_2\text{Br}$ is the rate determining step or whether a bimolecular reaction between the two mercury compounds is involved. This question is under active investigation. The initial product, I, apparently is stable at 80° and is able to react with a second mole of $\text{C}_6\text{H}_5\text{HgCCl}_2\text{Br}$ (or CCl_2). However, it is obvious from the products formed that CCl_2 insertion into the C-Hg bond of I appears to be much more facile than insertion into the Si-Hg linkage. The major product, $(\text{CH}_3)_3\text{SiCCl}=\text{CCl}_2$, suggests that an intermediate, II, is involved, in which two CCl_2 units separate silicon from mercury and from which $(\text{CH}_3)_3\text{SiHgCl}$ could be lost by a β -elimination process. Trimethylsilylmercuric chloride is not a stable compound and decomposes as shown in equation (5). This was shown by an attempt at its preparation by a disproportionation reaction in which bis(trimethylsilyl)mercury in benzene was treated with an equimolar amount of mercuric chloride at room temperature. Metallic mercury (88%) was formed in an exothermic reaction, and GLPC showed the solution to contain trimethylchlorosilane (95%).

Such reactions may provide a useful route to trihalovinyl derivatives of silicon and germanium, as well as of other elements, and metal- $\text{CH}=\text{CHX}$ systems may be accessible *via* analogous reactions of phenyl(dihalomethyl)mercury compounds. Studies designed to expand the scope of this new reaction are in progress.

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