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CX_2 insertion into the silicon–mercury and germanium–mercury bonds

The insertion of CCl_2 (generated *via* CCl_3CO_2Et + base) into the C–Hg bonds of dialkylmercury compounds, which gives products of type $RCCl_2HgR$, has been reported by Landgrebe and Mathis[1], and in these Laboratories we found that CCl_2 (generated *via* phenyl(bromodichloromethyl)mercury) will insert into mercury–halogen linkages to give $Hg{-}CCl_2X$ compounds[2]. 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 $C_6H_5HgCCl_2Br$[3] in 15 ml of benzene under argon at 65–75° was added 12.45 mmoles of bis(trimethylsilyl)mercury[4] 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, $(CH_3)_3SiCCl{=}CCl_2$**, 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 $C_6H_5CCl_2Br/(Me_3Si)_2Hg$

$$(Me_3Si)_2Hg + 2\,C_6H_5HgCCl_2Br \longrightarrow 2\,C_6H_5HgBr + Me_3SiCCl{=}CCl_2 + Me_3SiCl + Hg \qquad (1)$$

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 $C_6H_5HgCCl_2Br$ used, was 80%.

A reaction carried out in similar fashion with bis(trimethylgermyl)mercury[6] (9.2 mmoles) and phenyl(bromodichloromethyl)mercury (22.9 mmoles) in 70 ml of benzene resulted in formation of trimethylchlorogermane and trimethyl(trichlorovinyl)germane, $(CH_3)_3GeCCl{=}CCl_2$***, 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)mercury[3] (a CClBr source) in 1:2 ratio in refluxing benzene produced a silane believed to be $(CH_3)_3SiCCl{=}CClBr$**** in 37% yield. Reactions with $(Et_3Si)_2Hg$[7] and $(n\text{-}Bu_3Ge)_2Hg$ 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.

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

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

**** $\nu_{C=C}$ 1530 cm^{-1}; Me_3Si bands at 1255, 840 and 760 cm^{-1}. Analysis satisfactory. The alternate structure, $(CH_3)_3SiCBr{=}CCl_2$, is not excluded, but is considered less likely in terms of the mechanism proposed.

$$(Me_3Si)_2Hg + C_6H_5HgCCl_2Br \rightarrow \underset{\text{I}}{Me_3SiHgCCl_2SiMe_3} + C_6H_5HgBr \tag{2}$$

$$Me_3SiHgCCl_2SiMe_3 + C_6H_5HgCCl_2Br \rightarrow \underset{\text{II}}{Me_3SiHgCCl_2CCl_2SiMe_3} \tag{3}$$

$$Me_3SiHgCCl_2CCl_2SiMe_3 \rightarrow Me_3SiHgCl + Me_3SiCCl{=}CCl_2 \tag{4}$$

$$Me_3SiHgCl \rightarrow Me_3SiCl + Hg \tag{5}$$

Reaction (2) involves CCl_2 insertion into the Si–Hg bond in a manner similar to CCl_2 insertion into the C–Hg bond[1]. It is not yet clear whether this is a process in which decomposition of $C_6H_5HgCCl_2Br$ 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 $C_6H_5HgCCl_2Br$ (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, $(CH_3)_3SiCCl{=}CCl_2$, suggests that an intermediate, II, is involved, in which two CCl_2 units separate silicon from mercury and from which $(CH_3)_3SiHgCl$ 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-CH=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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