Preliminary Notes

Phenyl(dihalomethyl)mercury compounds

The reaction of organotin and organosilicon hydrides with (halomethyl)mercury compounds

We have reported[1] that the action of $C_6H_5HgCX_2Br$ ($X = Cl$ and Br) on triorganosilanes and on triphenylgermane results in dihalomethylenation* of the Si–H and Ge–H linkages. This note describes further experiments in this area which have bearing on the problem of the mechanism of the methylenation of Group IV element hydrides by mercurial reagents and which also are of interest from the synthetic standpoint.

The action of tri-*n*-butyltin hydride on phenyl(bromodichloromethyl)mercury[3] did not result in a methylenation reaction. Reduction of the C–Br linkage was observed rather than formation of $(C_4H_9)_2SnCHCl_2$.

$$(C_4H_9)_3SnH + C_6H_5HgCCl_2Br \longrightarrow (C_4H_9)_3SnBr + C_6H_5HgCHCl_2 \qquad (1)$$

Such a result is not too surprising in view of the known facile reduction of polyhalomethanes, especially those containing bromine, by tri-*n*-butyltin hydride[4]. The reaction above gave $C_6H_5HgCHCl_2$ in 60 % recrystallized yield when a 50 % excess of the hydride was allowed to react with the mercurial in benzene at room temperature during 3 hours, m.p. 69–71°. (Found: C, 23.36; H, 1.93; Cl, 19.67; Hg, 55.24; $C_7H_6Cl_2Hg$ calcd.: C, 23.25; H, 1.67; Cl, 19.61; Hg, 55.48 %.) NMR**: singlet at 6.00 p.p.m. (1H, –C*H*Cl$_2$), phenyl absorption (5H) at 7.32 p.p.m. Conversion of the tri-*n*-butyltin bromide which was produced to the insoluble fluoride (91 %) left an organic layer from which the dichloromethylmercurial could be isolated. Similar experiments, in which the exact stoichiometric quantity of tri-*n*-butyltin hydride was allowed to react with $C_6H_5HgCBr_3$ and with $C_6H_5HgCBr_2Cl$, did not proceed as well. As a rule, noncrystallizable oils resulted, but in a few instances crystalline solids were obtained from which could be isolated $C_6H_5HgCHBr_2$, m.p. 66.5–68.5°. (Found: C, 18.89; H, 1.55; Br, 35.01; Hg, 44.56. $C_7H_6Br_2Hg$ calcd.: C, 18.66; H, 1.34; Br, 35.48; Hg, 44.52 %.) NMR: singlet at 5.72 p.p.m. (1H, –C*H*Br$_2$), phenyl absorption (5H) at 7.21 p.p.m.; and $C_6H_5HgCHBrCl$, m.p. 64.5–66°. (Found: C, 20.51; H, 1.77; Hg, 49.37; $C_7H_6BrClHg$ calcd.: C, 20.70; H, 1.49; Hg, 49.41 %.) NMR: singlet at 5.87 p.p.m. (1H, –C*H*BrCl), phenyl absorption (5H) at 7.21 p.p.m., respectively. The yields of pure material in these instances was *ca.* 20 %.

In a recent publication Reutov and Lovtsova[5] reported the preparation of $C_6H_5HgCHCl_2$ (70 % yield) and $C_6H_5HgCHBr_2$ (20 %) by the reaction:

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* We use the term "methylenation" to describe the transfer of CZ_2 from one compound to another. It is not meant to have any mechanistic implications. This term was coined originally[2] to describe the formation of (halomethyl)metal derivatives by the reaction of diazomethane with metallic halides.

** NMR spectra were measured using a Varian Associates A60 NMR spectrometer. Chemical shifts are given in p.p.m. downfield from tetramethylsilane.

$$C_6H_5HgX + CH_2X_2 + (CH_3)_3COK \longrightarrow C_6H_5HgCHX_2 + KX + (CH_3)_3COH \qquad (2)$$

Although we had shown[3] that the reaction of phenylmercuric halide with haloforms and potassium *tert*-butoxide involves nucleophilic displacement of halide ion from mercury by CX_3^- to give $C_6H_5HgCX_3$, these authors expressed their preference for $:CHX$ insertion into the $C_6H_5Hg{-}X$ bond as the mechanism for reaction (2). Applying to this question the test which we had used in the case of the analogous haloform reaction[3], we have found that the reaction of phenylmercuric *bromide* with the methylene *chloride*/potassium *tert*-butoxide reagent system gives as $C_6H_5HgCHX_2$ product only the dichloromethyl compound (42 % recrystallized yield); none of the bromochloromethyl compound could be detected. In addition unreacted phenylmercuric bromide (37 %) was isolated and a lesser amount of diphenylmercury (a product which the Russian authors also found). The exclusion of exchange reactions as complicating factors[3] then leaves very little doubt that this reaction is one in which the CHX_2^- ion displaces X^- from mercury to give $C_6H_5HgCHX_2$, rather than a carbene insertion reaction[*].

The occurrence of reaction (1) suggested as a possible mechanism for the $R_3SiH/C_6H_5HgCX_2Br$ methylenation reaction[1] a reduction–alkylation sequence, *viz.*,

$$R_3SiH + C_6H_5HgCCl_2Br \longrightarrow R_3SiBr + C_6H_5HgCHCl_2$$

followed by

$$R_3SiBr + C_6H_5HgCHCl_2 \longrightarrow R_3SiCHCl_2 + C_6H_5HgBr$$

This possibility was excluded experimentally. Under the conditions of the observed methylenation reaction (4 h in refluxing benzene solution) no reaction occurred between triethylbromosilane and phenyl(dichloromethyl)mercury.

The iodomethylmercuric iodide/diphenylmercury reagent system[6] also was found to methylenate triethylsilane readily in refluxing benzene solution. A reaction (20 h) using 20 mmoles each of the mercury compounds, 100 mmoles of the silane and 40 ml of solvent resulted in the formation of triethylmethylsilane[7] in 83 % yield and phenylmercuric iodide in 93.5 % yield. Here also the reduction–alkylation sequence was excluded as a possible mechanism. The products which would result in a reduction reaction, methylmercuric iodide and triethyliodosilane, did not react in refluxing benzene solution under the conditions of our experiment.

Thus neither the methylenation nor the dihalomethylenation of silicon hydrides involves a reduction–alkylation sequence. Experiments designed to distinguish between a carbene insertion mechanism and a bimolecular CZ_2 transfer from mercurial to the silane are in progress. It is of interest to note that $:CH_2$ from photolysis of diazomethane in ether solution reacts readily with $C_6H_5SiH_3$ [to give $C_6H_5(CH_3)SiH_2$ in 70 % yield] and with $(C_6H_5)_2SiH_2$ [giving $(C_6H_5)_2Si(CH_3)H$ in 50 % yield], but that it reacts hardly at all with triethylsilane (triethylmethylsilane in 1 % yield) under comparable conditions[8].

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[*] It should be noted that the m.p. (84.5–86.5°) reported by ref. 5 for $C_6H_5HgCHBr_2$ is considerably higher than the one we give above. However, the Russian authors mention that a satisfactory analysis of their compound could not be obtained. The complete elemental analysis and also the integrated NMR spectrum of our product of m.P. 66.5–68.5° agrees excellently with its formulation as $C_6H_5HgCHBr_2$.

The practical[a] preparation of $C_6H_5HgCHCl_2$ opens the possibility of CHCl transfer by the mercurial route. Preliminary experiments have shown that phenyl(dichloromethyl)mercury reacts with cyclohexene in a sealed tube at 145° (60 h) to give a mixture of both 7-chlorobicyclo[4.1.0]heptane isomers[4] in *ca.* 60% yield. The chemistry of $C_6H_5HgCHX_2$ compounds is under intensive investigation in these Laboratories.

It should be noted especially that all experiments described above were carried out under an atmosphere of prepurified nitrogen.

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1 D. SEYFERTH AND J. M. BURLITCH, *J. Am. Chem. Soc.*, 85 (1963) 2667.
2 D. SEYFERTH, *Chem. Rev.*, 55 (1955) 1155.
3 D. SEYFERTH AND J. M. BURLITCH, *J. Am. Chem. Soc.*, 84 (1962) 1757.
4 D. SEYFERTH, H. YAMAZAKI AND D. L. ALLESTON, *J. Org. Chem.*, 28 (1963) 703.
5 O. A. REUTOV AND A. N. LOVTSOVA, *Dokl. Akad. Nauk. SSSR*, 154 (1964) 166.
6 D. SEYFERTH, M. A. EISERT AND L. J. TODD, *J. Am. Chem. Soc.*, 86 (1964) 121.
7 H. WESTERMARK, *Acta Chem. Scand.*, 9 (1955) 947; our infrared spectrum and refractive index agreed excellently with those given in this reference.
8 K. A. W. KRAMER AND A. N. WRIGHT, J. *Chem. Soc.*, (1964) 3604.

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[a] The Reutov-Lovtsova procedure[5] obviously is to be preferred over the tin hydride reduction method.

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Cyclobutadiene–metal complexes

Part III[*]. Cyclopentadienylation by ligand transfer

We recently described[1,2] the preparation of some cyclobutadiene–metal complexes by transfer of the tetraphenylcyclobutadiene ligand from (tetraphenylcyclobutadiene)palladium halides (I) onto other metals by reaction of (I) with metal carbonyls. We now report examples of the transfer of the cyclopentadienyl ligand from iron to palladium, nickel, cobalt and titanium, as well as the reverse reaction from titanium to iron. The compounds used as the cyclopentadienylating agents are the readily prepared[3] cyclopentadienyliron dicarbonyl dimer (II) or cyclopentadienyliron dicarbonyl bromide (III). Preliminary results indicate that this reaction proceeds

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[*] The previous papers in this series are those in refs. 1 and 2.