# Stepwise Reduction of Polyhalomethanes with Organosilicon Hydrides

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Stepwise reductions of geminal organic polyhalides have been reported recently by Lorenz and Becker,[1] by Seyferth and his co-workers[2] and by Kuivila and Menapace.[3] They all utilized organotin hydrides as reducing reagents and emphasis has been placed on that this is the best method available. In view of our recent discovery of the homolytic reduction of alkyl halides by organosilicon hydrides[4-6] it was logically thought that an alternative way of stepwise reduction employing this class of organometallic hydrides should be highly promising.

In the present investigation, a polyhalomethane was mixed with one half equivalent of triethylsilane or phenyldimethylsilane and heated in a sealed tube at 80°C for 10 hr in the presence of a catalytic amount of benzoyl peroxide. Identification of the reduction products was achieved by examining their physical properties (refractive indeces, retention times, infrared absorptions, *etc.*) after prior separation and purification by preparative scale v.p.c. The amounts of these products were determined by means of vapor phase chromatography. The quantities of the companion products, triethylsilyl or phenyldimethylsilyl halides, were not positively determined but the inspection of the vapor phase chromatograms showed that these were comparable with the comsumptions of the polyhalomethanes used. Results obtained from several repeated experiments are summarized in Table 1.

TABLE 1. REDUCTION OF POLYHALOMETHANES WITH ORGANOSILICON HYDRIDES

| Halide | Hydrosilane | Product[a] |
|---|---|---|
| $CCl_4$ | $Et_3SiH$ | $CHCl_3$ (98), $CH_2Cl_2$ (2) |
| $CHCl_3$ | $PhMe_2SiH$ | $CH_2Cl_2$ (94), $CH_3Cl$(−)[b] |
| $CBr_4$ | $Et_3SiH$ | $CHBr_3$ (94), $CH_2Br_2$ (6) |
| $CHBr_3$ | $Et_3SiH$ | $CH_2Br_2$ (100), $CH_3Br$ (−)[c] |
| $CH_2Br_2$ | $Et_3SiH$ | $CH_3Br$ (92), $CH_4$ (−)[b] |

a) Values in parentheses are yields based on the consumption of the respective starting materials.
b) Not determined.
c) Not detectable.

It is clearly seen that a polyhalide used as starting material gives an excellent yield of the reduction product arisen from the replacement of one of the halogen atoms originally present by hydrogen. This reduction does not take place to any appreciable extent in the absence of added initiator, so that there leaves little doubt that it involves free radical chain processes. The data in Table 1 also indicate the homolytic reduction of the polyhalomethanes to be increasingly facile in the orders:

$$R_3Si\cdot + R'X \rightarrow R_3SiX + R'\cdot$$
$$R'\cdot + R_3SiH \rightarrow R'H + R_3Si\cdot$$

chloroform < carbon tetrachloride; dibromomethane < bromoform < carbon tetrabromide. These tendencies can well be explained by reference to the reactivity sequence of polyhaloalkanes toward triorganosilicon free radicals.[5,6]

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