

Bis(triphenylsilyl)mercury

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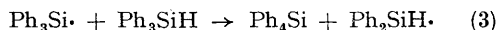
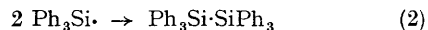
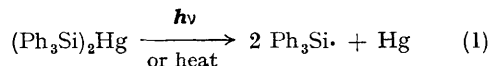
BIS(TRIMETHYLSILYL)MERCURY and bis(triethylsilyl)mercury can be prepared by the action of sodium amalgam on the organosilicon halide,¹ or by the reaction of diethylmercury with the organosilicon hydride.² Attempts to isolate the corresponding aromatic compounds have proved unsuccessful.^{1,3}

Bis(triphenylsilyl)mercury has now been prepared by the following method. A degassed solution of dibenzylmercury in triphenylsilane was heated at 165–168° for 2½ hr. The solution was filtered under nitrogen, cooled, and allowed to stand for two days, when pale cream crystals of bis(triphenylsilyl)mercury separated, m.p. 200–204° (decomp.). The identity of the compound was established on the basis of its quantitative decomposition into mercury and hexaphenyldisilane on heating *in vacuo*, and its infrared spectrum which showed the absence of aliphatic carbon–hydrogen bonds.

Bis(triphenylsilyl)mercury appears to be more stable than bis(triethylsilyl)mercury² to the air. The dry crystals may be exposed to the air for a short time without appreciable decomposition, but in the presence of organic solvents such as benzene, rapid decomposition takes place to give a complex mixture of products.

Bis(triphenylsilyl)mercury appears to be a

convenient thermal or photolytic source of triphenylsilyl radicals [compare bis(trimethylsilyl)mercury⁴]. Polymerisation of styrene was initiated by bis(triphenylsilyl)mercury on heating or illumination. Ultraviolet illumination of a solution of bis(triphenylsilyl)mercury in triphenylsilane gave hexaphenyldisilane, but pyrolysis of such a solution at 219° gave tetraphenyldisilane as the only solid product.



The radical transfer reaction (3) may be expected to have a higher activation energy than the combination reaction (2). Thus at high temperatures, the transfer reaction (3) can compete with the dimerization of the triphenylsilyl radicals (2), whereas the dimerization is the dominant process at the lower temperatures used in the photolytic experiments. Reactions of type (3) have been postulated⁵ to explain the radical-induced disproportionation of diphenylsilane to a mixture of silanes $\text{Ph}_n\text{SiH}_{4-n}$.

Triphenylsilane reacts with t-butyl peroxide on heating to give tetraphenylsilane as the only solid product. The t-butoxy-radicals produced by the pyrolysis of the peroxide presumably abstract hydrogen atoms from the triphenylsilane (reaction 4) and the resulting triphenylsilyl radicals react by reaction (3) to give the tetraphenylsilane.



This is in contrast to the behaviour of trialkylsilanes: trimethylsilane reacts with t-butylperoxide

to give t-butoxytrimethylsilane and hexamethyldisilane in comparable amounts. This implies that triphenylsilyl radicals do not react with the oxygen atoms in oxygen-containing compounds as readily as do trimethylsilyl radicals.⁶ This may be due to the inductive effect or the greater size of the phenyl groups, but it is also possible that there is some delocalization and stabilization in the triphenylsilyl radical which renders it less reactive than the trimethylsilyl radical.⁷

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