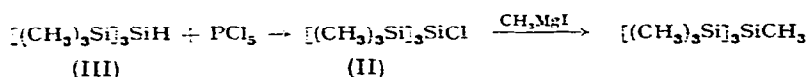


Highly branched-chain methylhalo polysilanes

Recently the preparation of the first *sym*-tetrasilylsubstituted silane, tetrakis(trimethylsilyl)silane (I), was reported¹. This compound has proven to be an important intermediate to branched polysilanes, and we are now reporting the synthesis and reactions of some halo polysilanes of this type. These were needed for the preparation of highly branched types to be used in various studies such as the acid catalyzed cleavage of the silicon group from the benzene and related cycles.

Tris(trimethylsilyl)chlorosilane (II) was prepared from (I) in a three-step synthesis. In accordance with a previously described procedure², (I) was reacted with methyl lithium and the resulting silyllithium solution was hydrolyzed with dilute acid to give tris(trimethylsilyl)silane (III). The reaction of (III) with phosphorus pentachloride in boiling petroleum ether (b.p. 60–70°) gave (II) in 50% yield, b.p. 70–72°/0.5 mm, m.p. 51–52° (Found: Cl, 12.50. C₉H₂₇ClSi₄ calcd.: Cl, 12.53 %.)

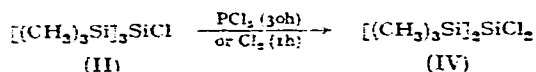


The structure of (II) was further confirmed by its reaction with methylmagnesium iodide to give the known² tris(trimethylsilyl)methylsilane (67.2%).

A more convenient preparation of (II) involves a halogen-hydrogen exchange reaction^{3,4} between carbon tetrachloride and (III). By this method, (II) was prepared in 80–90% yields by simply adding an excess of carbon tetrachloride to (III) and distilling off the excess reagent and chloroform over a 2 h period. Attempts to prepare (II) directly from the reaction of (I) with phosphorus pentachloride or chlorine⁵ were unpromising because the reaction was very slow, and secondary cleavages occurred to give higher chlorinated silanes.

In a reaction similar to that of (III) with carbon tetrachloride, 1-bromobutane was used to prepare tris(trimethylsilyl)bromosilane (79%), b.p. (sublimes) 80–90°/0.7 mm, m.p. 80–85°. (Found: Br, 24.46. C₉H₂₇BrSi₄ calcd.: Br, 24.58 %.) Reactions of this type with other silicon hydrides and alkyl or acyl halides have been reported³; however, aluminum chloride catalyst or long reflux periods were required.

Compound (II) reacts slowly with phosphorus pentachloride, and more rapidly with chlorine at a temperature that was maintained between –30° and –20°, to give 2,2-dichlorohexamethyltrisilane (IV), (70–76%), b.p. 76–77°/10 mm, $n_D^{20.3}$ 1.4800, $d^{20.3}$ 0.9708. (Found: Cl, 28.3; M_{RD} , 71.85. C₆H₁₈Cl₂Si₃ calcd.: Cl, 28.80%; M_{RD} , 71.46.)

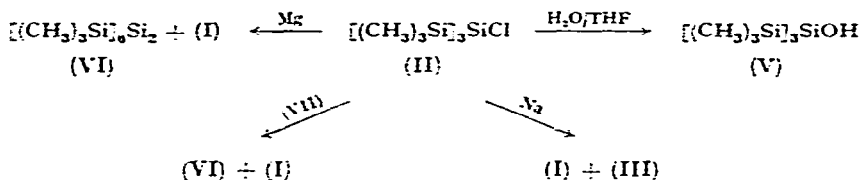


During both reactions, the disappearance of (II) was followed by vapor phase chromatography (VPC) to minimize secondary cleavage due to excess contact time with the chlorinating agent.

Treatment of (IV) with methylmagnesium iodide gave a previously described compound⁶⁻⁸, octamethyltrisilane (77.1%); and reduction with lithium aluminum hydride (LAH) gave bis(trimethylsilyl)silane (60.0%), b.p. 65°/45 mm, $n_D^{20.3}$ 1.4590,

$d^{20.3}$ 0.7620. (Found: MR_D , 63.31. Calcd.: MR_D , 63.60.) In addition to the usual infrared absorption for the $SiCH_3$ group, bands due to the $>SiH_2$ moiety⁹ appeared at 4.78μ and 10.96μ .

Hydrolysis of (II) with aqueous tetrahydrofuran (THF) afforded tris(trimethylsilyl)silanol (V) (67.6%), b.p. $81^\circ/1.5$ mm, $n_D^{20.3}$ 1.4990, $d^{20.3}$ 0.8668. (Found: MR_D , 89.60. Calcd.: MR_D , 89.39.)



In an attempt to prepare hexakis(trimethylsilyl)disilane (VI), compound (II) was coupled by the use of sodium or magnesium. The reaction with sodium gave a mixture of (I), (III) and small amounts of two unidentified compounds as the only products. The reaction with magnesium (catalyzed with ethyl iodide) gave a mixture of (VI) and (I). The known products were identified by VPC.

The reaction of (II) with tris(trimethylsilyl)silyllithium (VII) at room temp. and at 0° afforded a low yield (6–7%) of (VI), m.p. (in a sealed tube) $372\text{--}374^\circ$ dec. (Found: Si, 45.1. $C_{18}H_{54}Si_3$ calcd.: Si, 45.36%.) Compound (I) was the major product formed in this reaction (75%). The inability to obtain (VI) in higher yield in these reactions may be due to a combination of steric factors and the cleavage of (VI) by the silyl-metallic compound to give (I).

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