A New Route to Dimethylchlorosilane

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Summary A convenient preparation of dimethylchlorosilane by photolysis of polydimethylsilanes in the presence of hydrogen chloride is described.

DIMETHYLCHLOROSILANE, Me_2SiHCl (I), is one of the minor by-products from the "direct synthesis" of methylchlorosilanes,[1,2] but it is rather difficult to isolate pure because of unavoidable contamination by several by-products of similar b.p. such as tetramethylsilane and methyldichlorosilane. Eaborn *et al.*[3] recently reported a three-step preparation of (I) in 45% overall yield from dimethyldichlorosilane *via* partial dimethylamination, reduction with lithium aluminium hydride, and chloride-amination with hydrogen chloride.

We now report a convenient laboratory procedure for preparation of (I) by photolysis[4] in the presence of dry hydrogen chloride of dodecamethylcyclohexasilane or "polydimethylsilane" easily produced from sodium-condensation of dimethyldichlorosilane in boiling toluene.

A solution of dodecamethylcyclohexasilane[5,6] (8·0 g) in dry cyclohexane (200 ml) was irradiated at *ca.* 45° for 40 h with a low-pressure mercury lamp through a Vycor (or quartz) filter under bubbling dry hydrogen chloride (*ca.* 15 ml/min) admixed with nitrogen carrier. Volatile products were collected in two cold traps connected to the exit of the reaction vessel. Fractional distillation of the combined liquids from the vessel and traps gave 9·0 g (72%) of homogeneous (by g.l.c.) dimethylchlorosilane, b.p. 34—35° (lit.,[3,7] 34—36°).

Similarly, but with magnetic stirring, polydimethylsilane (15 g), which is a white powder, suspended in dry cyclohexane (400 ml) was irradiated for 55 h. As the reaction proceeded, the mixture became transparent. Distillation gave 14 g of pure (I).

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