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NOTE

ORGANOSILICON COMPOUNDS
XLIV*. CONVERSION OF DICHLORODIMETHYLSILANE INTO CHLORODIMETHYLSILANE

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There is at present no convenient laboratory procedure for partial reduction of organopolyhalogenosilanes to organomonohalogenosilicon hydrides. We have now devised a method for converting the readily available dichlorodimethylsilane into chlorodimethylsilane via chloro(dimethylamino)dimethylsilane. The procedure may possibly be of general utility in the preparation of organohalogenosilicon hydrides.

Dichlorodimethylsilane was converted into chloro(dimethylamino)dimethylsilane in 80% yield by treatment with dimethylamine in ether at −78° [2]. The chloro(dimethylamino)dimethylsilane was reduced with lithium aluminium hydride in ether to give (dimethylamino)dimethylsilane in 61% yield, and the latter was treated with anhydrous hydrogen chloride in dioxane to give chlorodimethylsilane in 92% yield. The overall yield from dichlorodimethylsilane was 45%.

The stability of the $Si{-}NMe_2$ bond towards lithium aluminium hydride, which is the key to the method, is consistent with its stability towards organolithium reagents[3].

EXPERIMENTAL

(Dimethylamino)dimethylsilane

A solution of chloro(dimethylamino)dimethylsilane (110 g, 0.8 mole), b.p. 106–108° [2], in ether (150 ml) was added slowly to a suspension of lithium hydride (9.5 g, 0.25 mole) in refluxing ether (300 ml). The reaction mixture was subsequently refluxed for a further 4 h, then cooled and filtered. Distillation of the filtrate gave (dimethylamino)dimethylsilane (51 g, 61%), b.p. 67°.

Chlorodimethylsilane

An excess of dry hydrogen chloride was bubbled through a solution of (dimethylamino)dimethylsilane (26 g, 0.25 mole) in anhydrous dioxane (100 ml) maintained at 0°. The white paste which formed initially later turned pale brown. On

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* For Part XLIII see ref. 1.

standing the mixture separated into two layers, a colourless upper liquid layer and a lower brown-coloured layer containing precipitated dimethylamine hydrochloride. With the mixture maintained at 0°, volatile products were removed under reduced pressure via cold traps cooled successively to −23°, −78°, −123° and −196°. The fractions collected at −78° and −123° were combined and distilled to give chlorodimethylsilane (22 g, 92%), b.p. 34–36° (lit.[4], 33–37°).

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