Stereochemistry of the Reduction of Boron Trichloride by an Optically Active Silane

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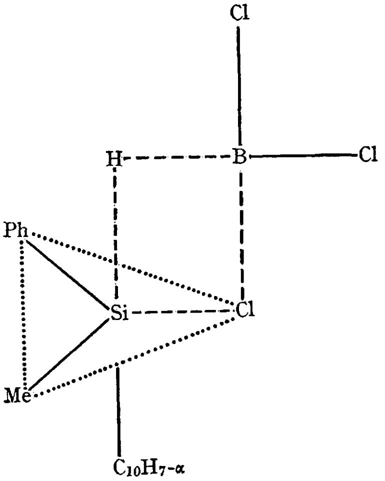
THE optically active silane, methyl-α-napththylphenylsilane, has already proved to be a powerful tool in the elucidation of a number of reaction mechanisms concerning silicon,[1] but the only reduction studied in this way has been that of triphenylmethyl chloride in a donor solvent.[2]

As part of a systematic study of the reducing properties of silanes, we have now found that methyl-α-naphthylphenylsilane reduces boron trichloride to diborane and is itself converted into the corresponding chlorosilane with at least 90% retention of configuration. Thus, (+)-methyl-α-naphthylphenylsilane ($[\alpha]_D^{20}$ + 34°) reacted with an excess of boron trichloride at room temperature to give diborane (98%), recovered boron trichloride, and (−)-methyl-α-naphthylphenylsilyl chloride (94%) ($[\alpha]_D^{20}$ −5·11°, lit.[1] $[\alpha]_D^{20}$ −6·2°). It is known that the (+)-silane and the (−)-chlorosilane are of the same absolute configuration.[1]

The 90% retention of configuration implies that Si–H bond scission and Si–Cl bond formation are synchronous as required by a four-centred reaction intermediate or transition state (see Figure). A similar four-centred mechanism has been suggested[2,3] for the reaction of triphenylmethyl chloride with silanes.

This result gives support to the tentative suggestion that the gas-phase reactions between methylchlorosilanes, Me_nSiHCl_{3-n} and boron halides may involve a four-centre mechanism.[4]



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