Thermal Racemization of the Optically Active Chlorosilane

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Incidentally to studies on chlorination of an optically active hydrosilane, (+)-α-naphthylphenylmethylsilane (I),[1] to the corresponding chlorosilane, (−)-α-naphthylphenylmethylchlorosilane (II), we have found that II was configurationally unstable at moderately high temperature (200—300°C) and recemized rather rapidly in the vapor phase as well as in the liquid state. Interestingly, I was configurationally more stable than II.

The optically active chlorosilane, II, mp 63. 8°C, $[\alpha]_D$ −6. 00(*c* 10. 68, cyclohexane)[lit.,[1] mp 63. 5—64°C, $[\alpha]_D$ −6. 28 (*c* 10. 5, cyclohexane)] was passed through a preparative g.l.c. (3 m column of Apiezon L grease on Celite 545) at 300°C with retention time of 35—50 min and recovered. Contrary to our expectation, the recovered II exhibited no optical rotation. However, I, mp 63. 7—64. 3°C, $[\alpha]_D$ +33. 7 (*c* 10. 9, cyclohexne) [lit.,[1] mp 63. 5—64. 5°C, $[\alpha]_D$ +34. 3 (*c* 10. 9, cyclohexane)], did not racemize under the same condition. Thus, I passed through the preparative g.l.c. at 300°C (retention time of 30—35 min) showed an optical activity, $[\alpha]_D$ +30. 5 (*c* 1. 40, cyclohexane). Accordingly, this figure indicates at least 95% retention of configuration of I.

To test that racemization of II proceeds non-catalytically, reactions were carried out in clean small sealed tubes. The results are listed in Table 1.

Obviously, II racemizes thermally even in the liquid state. Several possibilities responsible to racemization may be considered and elucidation of the mechanism is now in progress.

TABLE 1. THERMAL RACEMIZATION OF OPTICALLY ACTIVE CHLOROSILANE

No.	Wt. of II (g)	Temp. (°C)	Reaction time (min)	$[\alpha]_D$	Optical purity (%)
1	1. 085	200	65	−5. 54	92. 3
2	1. 054	250	65	−4. 74	79. 0
3	1. 136	300[a)]	67	−1. 06	17. 7

a) After the reaction, the sample colorized slightly, but an examination by g. l. c. showed that no detectable chemical change had occurred.

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[1] L. H. Sommer, "Stereochemistry, Mechanism, and Silicon," McGraw-Hill, New York (1965); L. H. Sommer, C. L. Frye, G. A. Parker and K. W. Michael, *J. Am. Chem. Soc.*, **86**, 3271 (1964); L. H. Sommer, C. L. Frye and G. A·Parker, *ibid.*, **86**, 3276, 3280 (1964); L. H. Sommer, *Angew. Chem.*, **76**, 176 (1962).