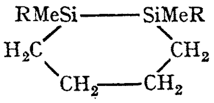
Preparation and Stereomutation of *cis*- and *trans*-1,2-Difluoro-1,2-dimethyl-1,2-disilacyclohexane

By K. TAMAO, M. ISHIKAWA, and M. KUMADA*

(*Department of Synthetic Chemistry, Kyoto University, Kyoto, Japan*)

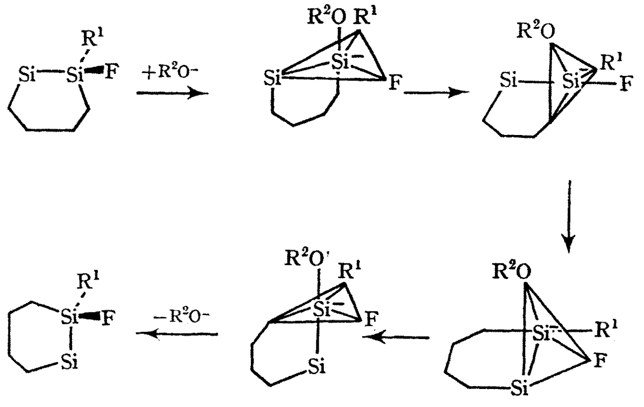
DURING our work on the stereochemistry of 1,1,2,2-tetrasubstituted 1,2-disilacyclohexane (I),[1] we prepared *cis*- and *trans*-1,2-difluoro-1,2-dimethyl-1,2-disilacyclohexane (Ib) and examined their chemical behaviour.



(Ia) R=Ph
(Ib) R=F

The phenyl derivative (Ia)[1] was dissolved in concentrated sulphuric acid in the cold and then treated with ammonium hydrogen fluoride,[2] to give the *cis*- and *trans*-isomers of the fluoro-derivative (Ib) in the ratio of *ca.* 1 : 1·9; treatment of the *cis*- or *trans*-isomer of (Ia), or a mixture of the two, gave the same ratio of products. The total yields were almost quantitative. The isomers were separated by preparative v.p.c., and identified by conversion into their phenyl derivatives (Ia). Thus, the isomer of (Ib) with the shorter retention time upon treatment with phenylmagnesium chloride in tetrahydrofuran gave *trans*-(Ia), while the other resulted in exclusive formation of both in excellent yields. Since the overall results of this phenylation involved no stereomutation, unambiguous correlations of configuration between (Ia) and (Ib) were achieved.

As expected, the fluoro-derivative (Ib) readily underwent stereomutation when shaken with concentrated sulphuric acid at room temperature to give an isomeric mixture in approximately the same molar ratio as described above. Furthermore, the very ready stereomutation of (Ib) was also effected by the addition of a small quantity of ethanol to n-hexane or benzene solutions of the compound at room temperature. Here again, an equilibrium mixture of *cis-* and *trans*-isomers in the ratio of about 1 : 1·9 was formed.



FIGURE

This behaviour is similar to that observed in the racemization of optically active α-naphthylphenylmethylfluorosilane[3] by the addition of methanol to solutions of the compound in pentane and t-butyl alcohol; a mechanism was suggested, which involved equilibrium formation of a pentacovalent-silicon intermediate, with the organic groups and the fluorine being basal in a tetragonal pyramid, and methoxide being apical. Although a similar tetragonal pyramidal intermediate may account for the stereomutation of our difluorodisilacyclohexane (Ib), a more attractive mechanism seems to involve pseudo-rotation[4] between trigonal–bipyramidal intermediates with a pentacovalent-silicon atom occupying the centre (see Figure). Since inspection of molecular models for the 1,2-disilacyclohexanes (I) reveals that there is internal strain, which can be reduced if at least one of the Si–Si–CH_2 bond angles become 90°; this occurs in the trigonal–bipyramidal intermediate.

This work was supported in part by Tokyo-Shibaura Electric Co., Ltd. and Nitto Electric Industrial Co., Ltd.

(*Received, November 18th,* 1968; *Com.* 1571.)

---

[1] Preceding Communication.
[2] M. Kumada and K. Tamao, *Adv. Organometallic Chem.*, 1968, **6**, 23.
[3] L. H. Sommer and P. G. Rodewald, *J. Amer. Chem. Soc.*, 1963, **85**, 3898.
[4] See, *e.g.* F. H. Westheimer, *Accounts Chem. Res.*, 1968, **1**, 70.