Resolution of an Asymmetric Cyclosilane: Stereospecific Substitution Reactions

By ROBERT J. P. CORRIU* and JOËL P. MASSE

(*Laboratoire de Chimie Organique Physique, Faculté des Sciences, 86-Poitiers, France*)

WHILST studying nucleophilic substitution reactions at a silicon atom, we have synthesized 2,2-dichloro-1,2,3,4-tetrahydro-2-silanaphthalene by an improved Vdovin and Nametkin's method.[1] This compound was transformed into 1,2,3,4-tetrahydro-2-methoxy-2-α-naphthyl-2-silanaphthalene by Grignard synthesis and has been resolved[2] with (−)-menthol as resolving agent. The optically active derivative obtained [(+)R_3Si-OMen] was used for a series of nucleophilic substitution reactions at the silicon atom. The compounds formed are optically active and have been compared with their racemic analogues.

These nucleophilic substitution reactions are highly stereospecific except the hydrolysis of the chlorosilane which racemises in all the ethereal solvents, and the reduction of the fluorosilane by lithium aluminium hydride.

Similar specific rotations of the silanes (Ia), (Ib), and (Ic), are obtained after a series of different reactions. Likewise, the two enantiomeric fluorosilanes (IIa) and (IIb) obtained by different synthetic routes have specific rotation values, similar but opposite. The methoxysilanes (IIIa) and (IIIb) show the same characteristics.

$$\underset{[\alpha]_D = +10^\circ}{(+)\text{-}R_3Si\text{-}OMen} \xrightarrow{AlH_4Li} \underset{[\alpha]_D = +21{\cdot}60^\circ}{(+)\text{-}R_3Si\text{-}H}\ \text{(Ia)}$$

$$\underset{[\alpha]_D = +10^\circ}{(+)\text{-}R_3Si\text{-}OMen} \xrightarrow{BF_3,\ Et_2O} \underset{[\alpha]_D = -34{\cdot}10^\circ}{(-)\text{-}R_3Si\text{-}F}\ \text{(IIa)}$$

$$\underset{[\alpha]_D = -34{\cdot}10^\circ}{(-)\text{-}R_3Si\text{-}F} \xrightarrow{AlH_4Li} \underset{\text{Racemic}}{R_3Si\text{-}H}$$

$$\underset{[\alpha]_D = +21{\cdot}60^\circ}{(+)\text{-}R_3Si\text{-}H} \xrightarrow{Cl_2\text{-}CCl_4} \underset{[\alpha]_D = +28{\cdot}50^\circ}{(+)\text{-}R_3Si\text{-}Cl}$$

$$\underset{[\alpha]_D = +21{\cdot}60^\circ}{(+)\text{-}R_3Si\text{-}H} \xrightarrow{KOH} \underset{[\alpha]_D\ \text{variable}}{R_3Si\text{-}OK}$$

$$R_3Si\text{-}OK \xrightarrow{MeCOCl} \underset{[\alpha]_D = +14^\circ}{(+)\text{-}R_3Si\text{-}O{\cdot}COMe}$$

$$R_3Si\text{-}OK \xrightarrow{Me_2SO_4} \underset{[\alpha]_D = +70^\circ}{(+)\text{-}R_3Si\text{-}OMe}\ \text{(IIIb)}$$

$$\underset{[\alpha]_D = +21{\cdot}60^\circ}{(+)\text{-}R_3Si\text{-}H} \xrightarrow{PhLi} \underset{[\alpha]_D = +130{\cdot}8^\circ}{(+)\text{-}R_3SiPh}$$

$$\underset{[\alpha]_D = +28{\cdot}50^\circ}{(+)\text{-}R_3Si\text{-}Cl} \xrightarrow{MeOH\text{-}C_6H_{12}NH_2} \underset{[\alpha]_D = -70^\circ}{(-)\text{-}R_3Si\text{-}OMe}\ \text{(IIIa)}$$

$$\underset{[\alpha]_D = +28{\cdot}50^\circ}{(+)\text{-}R_3Si\text{-}Cl} \xrightarrow{AlH_4Li} \underset{[\alpha]_D = -19^\circ}{(-)\text{-}R_3Si\text{-}H}\ \text{(Ib)}$$

$$\underset{[\alpha]_D = +28{\cdot}50^\circ}{(+)\text{-}R_3Si\text{-}Cl} \xrightarrow{H_2O\text{-}Et_2O} \underset{\substack{[\alpha]_D\ \text{variable} \\ \text{maximum}\ -48^\circ}}{(-)\text{-}R_3Si\text{-}OH}$$

$$\underset{[\alpha]_D = -70^\circ}{(-)\text{-}R_3Si\text{-}OMe} \xrightarrow{MeMgI} \underset{[\alpha]_D = -78{\cdot}90^\circ}{(-)\text{-}R_3Si\text{-}Me}$$

$$\begin{array}{ccc}(-)\text{-R}_3\text{Si–OMe} & \xrightarrow{\text{AlH}_4\text{Li}} & (-)\text{-R}_3\text{Si–H} \quad (\text{Ic}) \\ [\alpha]_D = -70^\circ & & [\alpha]_D = -20^\circ\end{array}$$

$$\begin{array}{ccc}(-)\text{-R}_3\text{Si–OMe} & \xrightarrow{\text{BF}_3,\ \text{Et}_2\text{O}} & (+)\text{-R}_3\text{Si–F} \quad (\text{IIb}) \\ [\alpha]_D = -70^\circ & & [\alpha]_D = +31{\cdot}40^\circ\end{array}$$

The relative configurations of these different products, whose optical purity is very high, are under study.

(*Received, October 23rd,* 1967; *Com.* 1131.)

---

[1] V. M. Vdovin and N. S. Nametkin, *Izvest. Akad. Nauk S.S.S.R.*, 1964, **154**, 987.

[2] L. H. Sommer, C. L. Frye, G. A. Parker, and K. W. Michael, *J. Amer. Chem. Soc.*, 1964, **86**, 327.