

THE STEREOSPECIFIC SYNTHESIS AND REARRANGEMENT OF AN  $\alpha$ -HYDROXYSILANE\*

A.G. Brook and C.M. Warner

Department of Chemistry, University of Toronto

(Received 28 May 1962)

THE recent exciting work of Sommer and Frye<sup>1,2</sup>, relating to optically active organosilicon compounds and their transformations involving either retention or inversion of configuration, have permitted us to extend these studies to the realm of optically active carbon-functional organosilanes with two immediately interesting results.

(a) Coupling of an optically active chlorosilane asymmetric at silicon with organometallic reagents can be made to occur stereospecifically, taking place, we believe, by inversion of configuration.

(b) Rearrangement of an optically active  $\alpha$ -hydroxysilane, asymmetric at silicon, to its isomeric silyl ether, is similarly stereospecific, occurring, we believe, with retention of configuration.

Since coupling of organometallics with organic halides is not a particularly useful synthetic reaction, there have been few studies of this reaction from the stereochemical point of view.<sup>3,4</sup> What evidence there is indicates, apart from racemization which may be the major stereochemical

---

\* This paper was presented in part at the 45th Annual Conference of the Chemical Institute of Canada, Edmonton, Alberta, May 28, 1962.

<sup>1</sup> L.H. Sommer and C.L. Frye, *J. Amer. Chem. Soc.* 81, 1013 (1959); *Ibid.* 82, 3796, 4118 (1960); L.H. Sommer, C.L. Frye *et al.*, *Ibid.* 83, 2210 (1961).

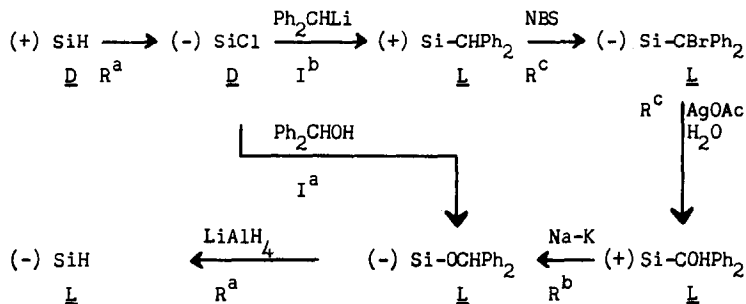
<sup>2</sup> C.L. Frye, Ph.D. Thesis, Pennsylvania State University, 1960, University Microfilms, Ann Arbor, Michigan.

<sup>3</sup> R.L. Letsinger, *J. Amer. Chem. Soc.* 70, 406 (1948); R.L. Letsinger and J.G. Trayham, *Ibid.* 72, 849 (1950).

<sup>4</sup> H.D. Zook and R.N. Goldey, *J. Amer. Chem. Soc.* 75, 3975 (1953).

course of the reaction, that such couplings occur by inversion. In our hands the coupling of optically active methylphenyl- $\alpha$ -naphthylchlorosilane with diphenylmethyl lithium and other organometallics appears to be essentially free of racemization, based on the ease of crystallization, and on the results of a sequence of reactions involving a Walden cycle.

The sequence of reactions outlined below constitutes a complete Walden cycle in which overall inversion has occurred. Four of these reactions involve the asymmetric silicon atom. On the basis of the stereochemical assignments of certain types of reaction by Sommer and Frye<sup>1,2</sup> and their general conclusions about the stereochemistry of reactions involving certain leaving groups, it is possible to make self-consistent stereochemical assignments for each step.



R = retention, I = inversion,  $\underline{\text{D}}$  = arbitrary configuration assigned to (+) SiH. Attached to silicon in each case are methyl, phenyl and  $\alpha$ -naphthyl.

- (a) Assignment by Sommer and Frye;
- (b) assignment this work;
- (c) reaction does not involve asymmetric centre.

Apart from the assignments of Sommer and Frye, which appear to be well-established, the stereochemistry of two steps in this sequence are unknown. Since overall inversion is observed in going from (-) SiCl to (-) SiOR (R = CHPh<sub>2</sub>) via the coupling and carbinol rearrangement, then either the

coupling is invertive and the carbinol-to-ether rearrangement is retentive or the reverse is true. On the basis of our belief that the rearrangement is intramolecular,<sup>5,6</sup> involving "flank" attack,<sup>7,8</sup> and hence is retentive, the coupling is therefore invertive, in accord with the findings of Letsinger<sup>3</sup> and of Zook<sup>4</sup>. In addition, this is in accord with the results of Sommer that all reactions involving displacement of chloride ion (a good leaving group) occur with inversion. Amongst those reported are hydride reduction, hydrolysis and alcoholysis.<sup>1,2</sup> That the rearrangement of the carbinol to its isomeric ether is retentive, gains support from a consideration of models of the compounds involved.

That overall inversion occurs in going from (-) SiCl to (-) SiOR is confirmed by the independent synthesis of the ether from (-) SiCl and benzhydrol using diisopropylamine, to give ether of the same sign of rotation as that observed by the other route. This reaction has been assigned an invertive course by Sommer<sup>1</sup>.

In other studies in progress it has been observed that couplings of organometallics with optically active SiCl or SiH of the same configuration give tetrasubstituted silane of the same sign. However, coupling with alkoxy silane of the same configuration gives tetrasubstituted silane of opposite sign of rotation, indicating the opposite stereochemical pathway in this reaction. If coupling with SiCl is invertive, then that with silyl ether is retentive, a reasonable route, since one might anticipate effective co-ordination of the organometallic with the ether-oxygen as part of the reaction path, which would facilitate frontside or retentive attack. Thus,

---

<sup>5</sup> A.G. Brook, J. Amer. Chem. Soc. 80, 1886 (1958).

<sup>6</sup> A.G. Brook, C.M. Warner and M.E. McGriskin, J. Amer. Chem. Soc. 81, 981 (1959).

<sup>7</sup> C. Eaborn, Organosilicon Compounds. Butterworths, London (1960).

<sup>8</sup> L.H. Sommer and O.F. Bennett, J. Amer. Chem. Soc. 79, 1008 (1959).

there is a striking parallel between the behavior with organometallics and the analogous reactions with lithium aluminum hydride as reported by Sommer:  $\text{SiCl}$  is reduced invertively by lithium aluminum hydride, but  $\text{SiOR}$  is reduced retentively by this reagent. Further details and work will be reported later.

Treatment of 12.12 g (0.043 mole) of methylphenyl- $\alpha$ -naphthylchlorosilane,  $[\alpha]_D^{22} -6.47$  (cyclohexane,  $c = 10.5$ ), [prepared by chlorination of methylphenyl- $\alpha$ -naphthylsilane,  $[\alpha]_D^{22} +33.2$  (cyclohexane,  $c = 6.8$ , 98 per cent optically pure based on Sommer and Frye's results)], with diphenylmethylolithium [prepared by refluxing overnight in ether 16.8 g (0.1 mole) of diphenylmethane and 71.5 ml of 1.4 N butyllithium (0.1 mole)] over 6 hr (reaction probably complete in 1 hr) at room temperature gave on workup 14.3 g (80 per cent) of methylphenyl- $\alpha$ -naphthyldiphenylmethylsilane, m.p. 123-125°,  $[\alpha]_D^{22} +17.52$  ( $\text{CHCl}_3$ ,  $c = 14$ ). Recrystallization of a portion from heptane gave material melting 123-125°,  $[\alpha]_D^{22} +17.89^\circ$ , ( $\text{CHCl}_3$ ,  $c = 14.5$ ). Bromination<sup>5</sup> with one equivalent of N-bromosuccinimide in carbon tetrachloride gave methylphenyl- $\alpha$ -naphthyldiphenylbromomethylsilane in 96 per cent yield, m.p. 155-158°,  $[\alpha]_D^{22} -55.5^\circ$  ( $\text{C}_6\text{H}_6$ ,  $c = 5.2$ ). Recrystallization of a portion from heptane gave material m.p. 156-158°,  $[\alpha]_D^{22} -56.5^\circ$  ( $\text{C}_6\text{H}_6$ ,  $c = 5.3$ ).

Hydrolysis of the  $-55.5^\circ$  bromide with silver acetate in benzene-acetone-water medium<sup>5</sup> gave a viscous gum,  $[\alpha]_D^{22} -7.54^\circ$  ( $\text{CHCl}_3$ ,  $c = 11.9$ ) which was crystallized with difficulty from pentane to give solid carbinol in 67 per cent yield, m.p. 139-142°,  $[\alpha]_D^{22} -8.40^\circ$  ( $\text{CHCl}_3$ ,  $c = 12.6$ ) or  $[\alpha]_D^{22} +16.7^\circ$  (ether,  $c = 3.0$ ). Recrystallization from pentane gave m.p. 143-146°,  $[\alpha]_D^{22} +18.34^\circ$  (ether,  $c = 3.87$ ). Isomerization of the  $+16.7^\circ$  carbinol in ether with a drop of sodium-potassium alloy<sup>5</sup> over 15 min gave 97 per cent benzhydryloxymethylphenyl- $\alpha$ -naphthylsilane, m.p. 84-85°,  $[\alpha]_D^{22} -3.40^\circ$  (ether,  $c = 16$ ). Recrystallization from pentane failed to alter the

m.p.,  $[\alpha]_D^{20} -1.32^\circ$  ( $C_6H_6$ ,  $c = 11.0$ ). Synthetic benzhydryloxymethylphenyl- $\alpha$ -naphthylsilane, prepared from chlorosilane,  $[\alpha]_D^{20} -6.44^\circ$  (cyclohexane,  $c = 15.7$ ) and an equivalent of benzhydrol, refluxed in toluene with 1.05 equivalents of diisopropylamine for 9 hr gave a partially racemized oil,  $[\alpha]_D^{22} -0.59^\circ$  ( $C_6H_6$ ,  $c = 23.6$ ). Chromatography on silica gel to remove impurities and several recrystallizations from pentane gave racemic silyl ether, m.p. 68-72 $^\circ$ , and slightly impure active silyl ether, m.p. 67-71.5 $^\circ$ , mixed melting point with the active ether from the rearrangement 68-74 $^\circ$ ,  $[\alpha]_D^{23} -1.21^\circ$  ( $C_6H_6$ ,  $c = 5.37$ ).

Finally, reduction of the benzhydryl ether with rotation  $[\alpha]_D^{20} -1.32^\circ$  with lithium aluminum hydride in dibutyl ether gave a crude reaction product of benzhydrol and methylphenyl- $\alpha$ -naphthylsilane,  $[\alpha]_D^{20} -25.5^\circ$  (cyclohexane,  $c = 4$ ) which on recrystallization from pentane gave 60 per cent benzhydrol and 33 per cent of the silane,  $[\alpha]_D^{20} -27.6^\circ$  (cyclohexane,  $c = 2.6$ ). Further recrystallization from pentane gave silane, m.p. 62-66 $^\circ$ ,  $[\alpha]_D^{24} -30.2^\circ$  (cyclohexane,  $c = 1.26$ ). Analytical results of key compounds agreed with theory and the infrared spectra of all compounds were consistent with their proposed structures as well as being identical to the spectra of the racemic modification, completed work which will be reported later.

It will be noted that the final silane isolated is about 90 per cent optically pure. In as much as this cycle involves four reactions at the asymmetric center and that "best purity" material was not employed in all steps, it must be concluded that each step involving the asymmetric center is essentially stereospecific, unaccompanied by racemization.

Acknowledgments - This work was supported in part by the National Research Council of Canada. We are indebted to Dow Corning Silicones Limited of Canada for a gift of chemicals.