raphy of the crude reduction product through a 26 × 0.5 in. column of silica gel with a 10% benzene–pentane solvent blend gave (−)-α-naphthylphenylmethylsilane (1.00 g; 0.0040 mol), with $[\alpha]_D$ −7.4° (*c* 5.1 in pentane).

Preparation of New Compounds. These were all prepared by standard procedures usually involving reaction of R_3Si^*Cl with R′Li. Table III lists some of their physical properties and appropriate analytical data.

Stereochemistry of Asymmetric Silicon. XX. Hydroxylation and Carbene Insertion Reactions of R_3Si^*H[1,2]

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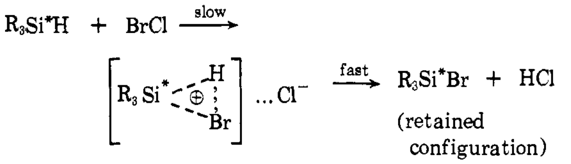
Abstract: Studies on the stereochemistry of the reactions of optically active R_3Si^*H (α-naphthylphenylmethylsilane) with perbenzoic acid (hydroxylation) to give R_3Si^*OH and with dihalocarbenes (insertion) to give R_3Si^*-CHX_2 are reported. Discussion of mechanism implications of this work leads to the conclusion that both reactions, like the halogenation of R_3Si^*H, involve three-center intermediates which give products with predominant retention of configuration.

In contrast to the preceding paper[2] in this series which dealt with strongly nucleophilic reagents such as KOH(s), $LiAlH_4$, and ROK, the present paper reports studies on R_3Si^*H using perbenzoic acid and halocarbenes. Both of the latter may be regarded as electrophilic in character. They are certainly *not* strong nucleophiles and the stereochemistry of their reactions with optically active R_3Si^*H is of mechanistic interest.

Hydroxylation of R_3Si^*H. Because of the close relationship we believe to exist between the hydroxylation described below and the reactions of R_3Si^*H with Cl_2, Br_2, and BrCl (uncatalyzed by light), it is perhaps appropriate to illustrate our preferred mechanism for halogenation of R_3Si^*H with BrCl as shown in eq 1.[3]



(1)

Based on mechanism model 1 we predicted and carried out the hydroxylation of R_3Si^*H with perbenzoic acid as the source of OH^+.

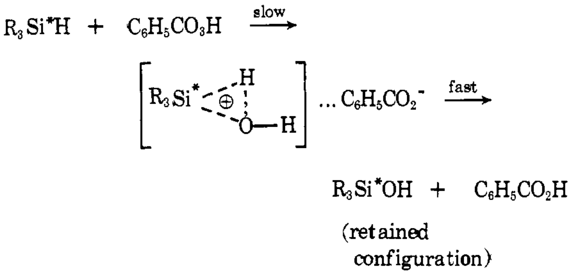
A 49% yield of optically active R_3Si^*OH was obtained from R_3Si^*H using an excess of perbenzoic acid in benzene solvent at room temperature for 12 hr. Pertinent data are given in reaction 2. The predominant stereo-

$$\underset{[\alpha]_D\ -35^\circ}{(+)R_3Si^*H} + C_6H_5CO_3H \longrightarrow \underset{[\alpha]_D\ -23^\circ}{(+)R_3SiOH} + C_6H_5CO_2H \quad (2)$$

chemistry of (2) is at least 93% retention of configuration based on an optical purity of the product of ∼86%. The method of calculating the per cent predominant stereochemistry has been reported.[4]

Since reaction 2 as formulated involves electrophilic attack on R_3Si^*H by OH^+, it had to be proven that the reaction is *not* in fact a nucleophilic substitution by benzoate anion followed by conversion of the formed benzoate (R_3Si^*OCOPh) to silanol. This latter possibility was excluded by experiments which showed that (a) (+)α-NpPhMeSiOCOPh gives no reaction with perbenzoic acid, and (b) work-up without the use of water still gives the silanol.

The simplest mechanism model for hydroxylation by reaction 2 is analogous to (1) and we have so formulated it in (3) below. Although more complex mechanisms



(3)

also are possible, we believe that all reasonable variants of (3) share with it the essential feature of electrophilic attack at the silicon–hydrogen bond.

Dihalocarbene Insertions into R_3Si^*H. There has recently been much interest in carbene (or carbenoid) insertions into Si–X bonds with which X = H,[5] C (ring strained),[6] and Cl.[7]

We wish to report stereochemical studies on such insertions[8] using optically active R_3Si^*H,[9] α-naphthylphenylmethylsilane.

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[1] Current support of this work by the National Science Foundation is gratefully acknowledged. Initial studies were carried out at the Pennsylvania State University with support from Dow Corning Corporation.

[2] For the preceding paper in this series, see: L. H. Sommer, W. D. Korte, and C. L. Frye, *J. Amer. Chem. Soc.*, **94**, 3463 (1972).

[3] L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill, New York, N. Y., 1965, pp 107–109.

[4] L. H. Sommer, J. D. Citron, and G. A. Parker, *J. Amer. Chem. Soc.*, in press.

[5] *Cf.* D. Seyferth and J. M. Burlitch, *ibid.*, **85**, 2667 (1963); K. A. Kramer and A. N. Wright, *J. Chem. Soc.*, 3604 (1963).

[6] D. Seyferth, R. Damrauer, and S. S. Washburne, *J. Amer. Chem. Soc.*, **89**, 1540 (1967).

[7] K. A. Kramer and A. N. Wright, *Angew. Chem.*, 74, 468 (1962).

[8] For a preliminary communication on this subject, see: L. H. Sommer, L. A. Ulland, and A. Ritter, *J. Amer. Chem. Soc.*, **90**, 4486 (1968).

[9] L. H. Sommer, C. L. Frye, G. A. Parker, and K. W. Michael, *ibid.*, **86**, 3271 (1964).

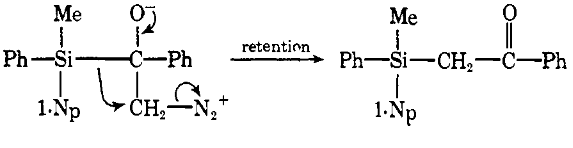
In particular, our work dealt with insertion into R_3Si^*H of CCl_2 and CBr_2 generated from the appropriate organomercury compounds, trichloro- and tribromomethylphenylmercury, $PhHgCX_3$.

It has been emphasized previously by Seyforth and coworkers[5] that the use of $PhHgCX_3$ for CX_2 insertion into Si–H is an especially useful method of carbene insertion because it avoids the use of strong bases that can give nucleophilic substitution with Si–H bonds. Thus, these reactions comprise a useful synthetic method and their stereochemical path and mechanism are therefore of considerable interest. Recent evidence furnished by Seyferth and coworkers has indicated that $PhHgCX_3$ functions as a source of free CX_2 carbene when heated.[10] Our interest in studying these insertions from a stereochemical viewpoint was derived from the obvious similarity of a three-center carbene insertion mechanism for Si–H to mechanism models 1 and 3 above.

In a recent elegant study, Brook and coworkers found that (*R*)-(+)-benzoyl-1-naphthylphenylmethylsilane[11] gave upon treatment with cold ethereal diazomethane in the dark for 14 days a 67% yield of I and a 33% yield of II, as formulated in reaction 4. Both products were

$$R_3SiCOR' + CH_2N_2 \longrightarrow \underset{\text{I}}{R_3SiCH_2COR'} + \underset{\text{II}}{R_3SiOCR'{=}CH_2} \qquad (4)$$

formed with predominant *retention* of configuration.[12] Formation of I is reasonably formulated as proceeding through intermediate III[12] and its tranformation to I likely proceeds *via* a three-center mechanism involving *electrophilic* attack on the silicon–acyl bond by the methylene group of the diazomethane, as follows



Thus, we anticipated (correctly, as it turns out) that a carbene-insertion mechanism for R_3Si^*–H should involve *retention* of configuration, and this work was done in part to test that hypothesis.

The general procedure used for dihalocarbene insertion into R_3Si^*H, following Seyferth and coworkers,[5] comprised refluxing a benzene solution of the silane and organomercury compound. This procedure gave $R_3Si^*CHX_2$ of good purity as determined by infrared and nmr spectra and analysis for C, H, and X. Using dextrorotatory R_3Si^*H, the insertions proceeded as follows.

$$\begin{array}{lll} (+)R_3Si^*H + PhHgCX_3 \longrightarrow & (+)R_3Si^*CHX_2 & (5) \\ [\alpha]_D +35^\circ & X = Cl;\ [\alpha]_D +21.0^\circ & \\ & X = Br;\ [\alpha]_D +14.3^\circ & \end{array}$$

The task of establishing the stereochemical path for reactions 5 involved solution of the problem of correlation of configuration between R_3Si^*H and R_3Si^*-CHX_2. This problem was solved by independent syntheses of $R_3Si^*CHX_2$ involving reactions of known stereochemistry. The latter used organolithium reagents in coupling reactions with R_3Si^*Cl, a class of reactions known to proceed with inversion of configuration,[13] in accord with the S_N2-Si stereochemistry rule of inversion of configuration for good leaving groups in R_3Si^*X.[14]

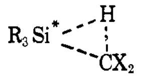
The dichloromethyllithium reagent was prepared in THF solvent by the general low-temperature method previously reported for α-chloroalkyllithium compounds.[15] Reaction of dichloromethyllithium with dibromomethane in THF solvent gave dibromomethyllithium. Correlations of configuration were achieved by reaction sequences 6. Thus, based on reasonable

$$\begin{array}{lll} (-)R_3Si^*H + Cl_2 \xrightarrow{\text{retention}} & (+)R_3Si^*Cl \xrightarrow[\substack{LiCHX_2 \\ -90^\circ}]{\text{inversion}} & \\ [\alpha]_D -35.2^\circ & [\alpha]_D +6.3^\circ & \\ & \qquad (+)R_3Si^*CHX_2 & (6) \\ & \qquad X = Cl;\ [\alpha]_D +22.6^\circ & \\ & \qquad X = Br;\ [\alpha]_D +13.8^\circ & \end{array}$$

assignment of an inversion stereochemistry to the coupling reactions of $LiCHX_2$, $(+)R_3Si^*CHCl_2$ and (+)-$R_3Si^*CHBr_2$ have the same configuration as $(+)R_3Si^*H$ and *the insertion of CCl_2 and CBr_2 into the silicon–hydrogen bond* proceeds *with predominant retention of configuration.*[16] The solid $R_3Si^*CHCl_2$ from the coupling reactions was recrystallized up to constant rotation, $[\alpha]_D +24.4^\circ$, thus indicating that the insertion reactions 5 proceeded with a predominant stereochemistry[4] of ~93% retention of configuration.

The insertion products of R_3Si^*H and those obtained by coupling reactions of $LiCHX_2$ with R_3Si^*Cl had identical infrared and nmr spectra. Especially for the formation of $R_3Si^*CHBr_2$, the spectral data and analyses show that, in its formation by the coupling reaction, the actual reaction did *not* involve prior decomposition of $LiCHBr_2$ to CHBr followed by insertion into R_3Si^*–Cl to give $R_3Si^*CHBrCl$.

The finding of a retention stereochemistry for the insertion reactions of CCl_2 and CBr_2 with R_3Si^*–H is certainly consistent with a three-center mechanism involving direct electrophilic attack of CX_2 on the silicon–hydrogen bond as in (7). Mechanism 7 pro-



(7)

ceeding *via* retention of configuration is analogous to (3) for hydroxylation and (1) for halogenation of R_3Si^*H, and is consistent with the mechanism proposed in an independent study by Seyferth and coworkers on the basis of kinetic evidence.[17]

Experimental Section

Reactions of Peroxybenzoic Acid with α-Naphthylphenylmethylsilanes. A. Without Added Cyclohexylamine. To a 125-ml erlenmeyer flask were added 10 ml of benzene and 0.86 g (3.5 mmol)

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[10] D. Seyferth, J. Y.-P. Mui, and J. M. Burlitch, *J. Amer. Chem. Soc.*, **89**, 4953 (1967).

[11] A. G. Brook and W. W. Limburg, *ibid.*, **85**, 832 (1963); A. G. Brook, C. M. Warner, and W. W. Limburg, *Can. J. Chem.*, **45**, 1231 (1967).

[12] A. G. Brook, D. M. MacRae, and W. W. Limburg, *J. Amer. Chem. Soc.*, **89**, 5493 (1967).

[13] For many examples, see L. H. Sommer, W. D. Korte, and P. G. Rodewald, *ibid.*, **89**, 862 (1967).

[14] L. H. Sommer, G. A. Parker, N. C. Lloyd, C. L. Frye, and K. W. Michael, *ibid.*, **89**, 857 (1967).

[15] D. F. Hoeg, D. I. Lusk, and A. L. Crumfliss, *ibid.*, **87**, 4147 (1965). Our procedure (see Experimental Section) employed −90° instead of −100° as reported.

[16] This conclusion is in nice accord with other findings reported subsequent to ref 8: A. G. Brook, J. M. Duff, and D. G. Anderson, *J. Amer. Chem. Soc.*, **92**, 7567 (1970).

[17] D. Seyferth, R. Damrauer, J. Y.-P. Mui, and T. F. Jula, *ibid.*, **90**, 2944 (1968).

of (−)-α-naphthylphenylmethylsilane, $[\alpha]_D$ −34.5° (*c* 2.2, in pentane). To the silane solution was added 30 ml of a 0.13 *N* benzene solution of peroxybenzoic acid (4.0 mmol). There was no evidence of any reaction. A 10-ml aliquot of the solution was pipetted into a 2.5-dm polarimeter tube; the observed rotation was −0.53°. The rotation slowly became more positive and after 5 hr reached a constant value of −0.29°. The benzene solutions were then combined, transferred to a separatory funnel, and washed five times with 10% aqueous sodium bicarbonate. Finally, the benzene solution was washed twice with cold water and dried over anhydrous sodium sulfate. Solvent removal at reduced pressure afforded 0.45 g (49% yield) of (−)-α-naphthylphenylmethylsilanol, $[\alpha]_D$ −23° (*c* 1.9, in benzene). The infrared spectrum (neat) of the product showed strong OH maxima (2.8, 3.0 μ) as well as some carbonyl absorption (5.9 μ) due to either peroxybenzoic acid or benzoic acid impurity. However, the amount of carbonyl was small.

B. With Added Cyclohexylamine. To a 125-ml erlenmeyer flask was added 0.50 g (2.0 mmol) of (−)-silane, $[\alpha]_D$ −29° (*c* 3.8, in pentane). To this solution was added 25 ml of a *ca.* 0.04 *N* benzene solution of peroxybenzoic acid (*ca.* 1 mmol). The flask was well stoppered, and the reaction was allowed to proceed overnight. During this time the solution became dark colored. The benzene solution was poured into a 250-ml suction flask and pentane (60 ml) was added. Then cyclohexylamine (1.0 ml, 8.3 mmol) was added to precipitate any peroxybenzoic or benzoic acids in the solution. Within a few seconds after the addition of the amine, a light colored precipitate formed. After 10 min, the solid was filtered from the solution; the pentane was then removed on a steam bath. Finally, benzene and unreacted amine were removed at 1 mm pressure and 90°. A dark oil (0.27 g) was obtained having $[\alpha]_D$ −18° (*c* 3.2, in pentane). The infrared spectrum (neat) of the product showed large amounts of both starting material (4.7 μ) and silanol (2.8, 3.0 μ). There was no maximum at 5.9 μ, so apparently the amine was effective in removing the carbonyl containing compounds. Since no water was used in the work-up, the silanol obtained must have been formed directly from the silane and peroxy acid; the silanol could not be a hydrolysis product.

Attempted Reaction with α-Naphthylphenylmethylbenzoxysilane. (+)-α-NpOMeSiOBz (1.12 g, 3.0 mmol) having [a $\alpha]_D$ +9.7° (*c* 8.1, in hexane) was dissolved in 10 ml of hexane in 2.5-dm polarimeter tube. The observed rotation was +1.97°. Then 15 ml of a 0.13 *N* benzene solution of peroxybenzoic acid (2.0 mmol) was added to the polarimeter tube. The observed rotation dropped to +0.77° due to the dilution by the peroxy acid solution. The rotation remained unchanged for 3 days. This indicates that there is no reaction between the (+)-benzoxysilane and peroxybenzoic acid.

Reaction of (+)R_3Si^*H with $PhHgCCl_3$. In a 250-ml flask a solution of 12.5 g (32 mmol) of $PhHgCCl_3$[18] and 8.0 g (32 mmol) of (+)-α-naphthylphenylmethylsilane, $[\alpha]_D$ +35.0° (*c* 4.0, in pentane), in 100 ml of anhydrous benzene was made up and then refluxed under a nitrogen atmosphere for 48 hr. The solution was then filtered free of precipitated phenylmercuric chloride (8.5 g, 86%), and the benzene solvent removed under vacuum. The remaining oil was taken up in 100 ml of pentane, and this solution was filtered from insoluble, unreacted $PhHgCCl_3$ and the solvent stripped off. The crude oil was then taken up in CCl_4, and Cl_2 was bubbled into the solution for 10 min to convert unreacted (+)R_3Si^*H to the chlorosilane. The CCl_4 was stripped off; the yellow oil was taken up in pentane and then washed with water to hydrolyze the chlorosilane to the silanol. The organic layer was dried over Na_2SO_4, stripped of solvent, and chromatographed on a 1.9 × 50 cm silica gel column with elution by 90% pentane–10% benzene (v/v), yielding 3.0 g (28%) of a clear, viscous oil, $[\alpha]_D$ +21.0° (*c* 5.0, in pentane). Infrared and nmr spectra of this oil in CCl_4 were consistent with the structure of $R_3SiCHCl_2$. The nmr spectrum was comprised of the following peaks in addition to downfield aromatic resonances: singlet at δ 0.90 ($SiCH_3$), and singlet at δ 5.87 ($SiCHCl_2$). The relative areas of these two peaks were 3 and 1, respectively.

Anal. Calcd for $C_{18}H_{16}Cl_2Si$: C, 65.26; H, 4.87; Cl, 21.40. Found: C, 64.39; H, 5.07; Cl, 21.00.

Reaction of (+)R_3Si^*H with $PhHgCBr_3$. Similar to the preceding experiment, 17.5 g (33 mmol) of $PhHgCBr_3$ and 8.3 g (33 mmol) of (+)-α-naphthylphenylmethylsilane, $[\alpha]_D$ +35.0° (*c* 4.0, in pentane), were combined in 150 ml of anhydrous benzene, and the solution was refluxed for 4 hr. Product isolation was achieved in a manner identical with the preceding experiment, yielding 8.0 g (57%) of a yellow viscous oil, $[\alpha]_D$ +14.3° (*c* 5.5, in pentane). The infrared and nmr spectra of this material in CCl_4 were consistent with those of $R_3SiCHBr_2$. The nmr spectrum was comprised of the following peaks in addition to downfield aromatic resonances: singlet at δ 0.93 ($SiCH_3$) and singlet at δ 5.70 ($SiCHBr_2$). The relative areas of these two peaks were 3 and 1, respectively.

Anal. Calcd for $C_{18}H_{16}Br_2Si$: C, 51.45; H, 3.84; Br, 38.03. Found: C, 51.71; H, 4.07; Br, 38.46.

Reaction of Dichloromethyllithium with (+)R_3Si^*Cl. Into a 500-ml flask equipped with a mechanical stirrer, dropping funnel, and nitrogen inlet tube were added 250 ml of dry THF (distilled from $LiAlH_4$) and 8.5 g (100 mmol) of methylene chloride. The vessel was immersed in a liquid nitrogen–toluene slush bath (−95°). When the temperature of the solution had reached −90°, 80 mmol of *n*-butyllithium in 50 ml of hexane was added over a 40-min period, and the solution was stirred 2 hr at −90°. To this resultant solution of dichloromethyllithium[15] was then added 22.6 g (80 mmol) of (+)-α-naphthylphenylmethylchlorosilane, $[\alpha]_D$ +6.3° (*c* 1.5, in pentane), in 50 ml of hexane over a 5 min period while maintaining the solution temperature below −80°. The solution was stirred an additional 4 hr, the contents then poured onto a slurry of ice, dilute HCl, and pentane, and the organic layer washed three times with water, dried over Na_2SO_4, and then stripped of solvent, yielding a viscous oil. This material was chromatographed over a column of silica gel with elution by 90% pentane–10% benzene (v/v), affording 21.2 g (82%) of a yellow oil. A second chromatography of this material gave 10 g of colorless oil which, on standing, crystallized into a white solid, mp 68–70°, $[\alpha]_D$ +22.6° (*c* 2.0, in pentane). The infrared and nmr spectra were identical with the spectra of the (+)$R_3SiCHCl_2$ obtained from reaction of (+)R_3Si^*H with $PhHgCCl_3$ reported above. The nmr spectrum included the singlet at δ 0.90 ($SiCH_3$) and the singlet at δ 5.88 ($SiCHCl_2$) characteristic of $R_3SiCHCl_2$.

Anal. Calcd for $C_{18}H_{16}Cl_2Si$: C, 65.26; H, 4.87; Cl, 21.40. Found: C, 65.25; H, 4.97; Cl, 21.32.

Reaction of Dibromomethyllithium with (+)R_3Si^*Cl. A solution of dichloromethyllithium in THF was prepared in the manner described in the preceding experiment. To this solution was added 17.4 g (100 mmol) of methylene bromide over a 5-min period, followed with stirring at −90° for 1.5 hr. To this resultant solution of dibromomethyllithium at −90° was then added slowly over 5 min a solution of 17 g (60 mmol) of (+)R_3Si^*Cl, $[\alpha]_D$ +6.3° (*c* 1.5, in pentane), in 40 ml of hexane, and stirring was continued at −90° for 4 hr. The reaction mixture was then worked up in a manner identical with that described in the previous experiment, yielding 20.6 g (82%) of a light brown oil, $[\alpha]_D$ +13.8° (*c* 3.5, in pentane). The infrared and nmr spectra were identical with the spectra of (+)$R_3SiCHBr_2$ obtained from reaction of (+)-R_3SiH and $PhHgCBr_3$ reported above. The nmr spectrum included the singlet at δ 0.93 ($SiCH_3$) and the singlet at δ 5.68 ($SiCHBr_2$) characteristic of $R_3SiCHBr_2$.

Anal. Calcd for $C_{18}H_{16}Br_2Si$: C, 51.45; H, 3.84; Br, 38.03. Found: C, 51.64; G, 4.00; Br, 38.48.

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(18) D. Seyferth and J. Burlitch, *J. Organometal. Chem.*, 4, 127 (1965). For a new and more convenient procedure for $PhHgCX_3$, published after our work was completed, see D. Seyferth and R. Lambert, Jr., *ibid.*, 16, 21 (1969).