β-2-Chlorothioxanthen-9-ol 10-Oxide (5β).—*m*-Chloroperbenzoic acid (0.69 g, 4.0 mmoles) dissolved in acetone (75 ml) was added to a stirred solution of **4** (1.0 g, 4.0 mmoles) in acetone (50 ml) at 0°. After 11 hr at 0° the reaction mixture was worked up as described for 2β to afford 0.5 g (1.89 mmoles, 47%) of 5β, mp 192–194°. Thin layer chromatography of the initially isolated reaction product showed the presence of three compounds: 2 chlorothioxanthone (*ca.* 15%), 5α (*ca.* 5%), and 5β (*ca.* 80%).[26] The infrared spectrum of 5β exhibited absorption at 1010, 1031, 1071, and 1100 cm^{-1}.[23]

Anal. Calcd for $C_{13}H_9ClO_2S$: C, 58.98; H, 3.43; S, 12.11; Cl, 13.39. Found: C, 59.13; H, 3.50; S, 11.90; Cl, 13.46.

Registry No.—2α, 13096-56-5; 2β, 13096-57-6; **3**, 6783-74-0; **4**, 6470-02-6; 5α, 13096-60-1; 5β, 13096-61-2.

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[26] The different stereoselectivities noted in the synthesis of 2β and 5β appear to reflect a dependence upon concentration and not simply upon differences between **3** and **4**.

Group VIII Metal Catalyzed Reactions of Organosilicon Hydrides with Amines, Hydrogen Halides, and Hydrogen Sulfide

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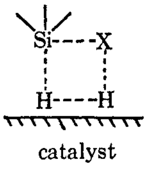
The stereochemistry and synthetic utility of the group VIII noble metal catalyzed reactions of silicon–hydrogen bonds with nonhydroxyllic compounds containing active hydrogen have been studied. The reaction provides a quick, convenient method for preparation of silylamines, silanethiols, and halosilanes. Various catalysts have been evaluated from both a preparative and a stereochemical viewpoint.

The group VIII metal catalyzed reaction of silanes containing a silicon–hydrogen bond with a hydroxyl group has been extensively studied.[1] However, there are very few reported reactions[2,3] between the silicon–hydrogen linkage and other compounds containing active hydrogen. We therefore undertook a study of the utility of this reaction for placing various nonoxygenated groups on silicon (eq 1), while simultaneously investigating the stereochemistry of the transformation.

$$\mathrm{R_3SiH + HX\cdots \xrightarrow{catalyst} R_3SiX\cdots + H_2} \qquad (1)$$

Since optically active α-naphthylphenylmethylsilane (R_3Si^*H) is readily available,[4] it was used to study both the synthetic utility and the stereochemistry of the reaction (Table I). The most striking result in Table I is that many of the reactions proceed with *inversion*. This result has also been found for oxygen functions.[1] This stereochemical result would seem to rule out the operation of a four-center mechanism such as **1** in these cases.



1

There are other interesting stereochemical points in Table I. An alumina support always gave better stereochemical results (reactions 1, 4, 12, 15, and 18) than a carbon support (2, 3, 10, 14, and 16), which gave racemic product in the aminosilane cases. This was not caused by the extra 5% palladium on the surface since 5% Pd–C also gave racemic product in reaction 5. Conversely, the carbon-supported catalyst appeared to be more active in the amine reactions.

The retention stereochemistry observed for HCl and H_2S is hard to rationalize. For instance, acid strength does not give a correlation, since hydrogen fluoride, which reacts with inversion, is intermediate between the two in acidity. The only similarity between both reagents seems to be that chlorine and sulfur are both second-row elements, but this may merely be a coincidence. More information concerning what takes place on catalyst surfaces is necessary before the mechanism of this reaction can be known with any degree of certainty.

To our knowledge, metal-catalyzed reactions of hydrogen halides or sulfur compounds with silicon–hydrogen bonds had not been reported previously and it was of interest to study this reaction in some detail. In Table II are found the results of reactions with triethylsilane. These results clearly show that this is a good method for preparation of halosilanes from compounds having a silicon–hydrogen bond. For chloro- and bromosilanes this may not offer much of an advantage over the reaction using the elemental halogen.[5,6] However, if there are organic groups present which can be halogenated by chlorine[6] but not by hydrogen chloride, the catalytic method may be advantageous.

In the case of fluorosilanes, the situation is different—direct halogenation is impossible.[5] The usual methods[7] involve replacement of chloride by fluoride using reagents such as ammonium fluoride and zinc fluoride or

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(1) L. H. Sommer and J. Lyons, *J. Am. Chem. Soc.*, **89**, 1521 (1967).

(2) L. Birkofer, E. Bierwirth, and A. Ritter, *Chem. Ber.*, **94**, 821 (1961).

(3) J. C. Saam and J. L. Speier, *J. Org. Chem.*, **24**, 119 (1959).

(4) L. H. Sommer, C. L. Frye, G. A. Parker, and K. W. Michael, *J. Am. Chem. Soc.*, **86**, 3271 (1964).

(5) V. Bazant, V. Chvalovsky, and J. Rathousky, "Organosilicon Compounds," Vol. I, Academic Press Inc., New York, N. Y., 1965, p 29.

(6) C. Eaborn, "Organosilicon Compounds," Butterworth London, 1960, pp 168–169, 209–210.

(7) Reference 6, pp 174–176.

TABLE I

GROUP VIII METAL CATALYZED REACTIONS OF (−)-R_3Si^*H WITH VARIOUS REAGENTS

Reaction	Reagent	Catalyst	Product, $[\alpha]_D$	Stereospecificity, %[a]	Yield, %
1	Pyrrolidine	5% Pd-Al_2O_3	(+)-R_3Si^*Pyr, 23.4°	Inversion, 100	87
2	Pyrrolidine	10% Pd–C	(±)-R_3Si^*Pyr, 0°	Racemic	..
3	Pyrrolidine[b]	10% Pd–C	(±)-R_3Si^*Pyr, 0°	Racemic	70
4	*i*-$BuNH_2$	5% Pd-Al_2O_3	(+)-R_3Si^*NHBu, 5.2°	Inversion, 100	84
5	*i*-$BuNH_2$	5% Pd–C	(±)-R_3Si^*NHBu, 0°	Racemic	..
6	*i*-$BuNH_2$	5% Pt–C	No reaction	...	..
7	*i*-$BuNH_2$	5% Rh–C	No reaction	...	..
8	*i*-$BuNH_2$	5% Rh-Al_2O_3	No reaction	...	..
9	*i*-$BuNH_2$	5% Ru–C	No reaction	...	..
10	*i*-$BuNH_2$[b]	10% Pd–C	(±)-R_3Si^*NHBu, 0°	Racemic	76
11	*i*-$BuNH_2$	Raney Ni[c]	No reaction	...	..
12	CH_3NH_2	5% Pd-Al_2O_3	(+)-$R_3Si^*NHCH_3$, 2.7°	Inversion, 69	58[d]
13	HF	5% Pd-Al_2O_3	(+)-R_3Si^*F, 30.6°	Inversion, 83	54
14	HF	10% Pd–C	(+)-R_3Si^*F, 25.6°	Inversion, 77	66
15	HCl	5% Pd-Al_2O_3	(+)-R_3Si^*Cl, 4.2°	Retention, 82	95
16	HCl	10% Pd–C	(+)-R_3Si^*Cl, 2.2°	Retention, 68	89
17	HCl	Charcoal	No reaction	...	..
18	H_2S	5% Pd-Al_2O_3	(+)-$R_3Si^*S^-\ ^+H_2NEt_2$, 36.5°	Retention, 84	11
19	H_2S	10% Pd–C	$R_3Si^*S^-\ ^+H_2NEt_2$	*e*	1
20	CH_3SH[f]	10% Pd–C	No reaction	...	..

[a] A stereospecificity of say 80% means that the product was 60% optically pure and 40% racemic. [b] Run in CH_2Cl_2. [c] Approximately 0.4 g of catalyst used. [d] Yield after first crystallization. [e] Not enough material for a rotation. [f] Procedure the same as for reactions 18 and 19.

TABLE II

GROUP VIII METAL CATALYZED REACTIONS OF TRIETHYLSILANE

Reaction	Reagent	Catalyst	Product	Yield, %
21	HF	5% Pd–C	Et_3SiF	78
22	HCl	5% Pd–C	Et_3SiCl	85
23	HCl	5% Rh–C	Et_3SiCl	100[a]
24	HCl	5% Ru–C	Et_3SiCl	100[a]
25	HCl	5% Pt–C	Et_3SiCl	100[a]
26	HCl	H_2PtCl_6	No reaction	...
27	H_2S	5% Pd-Al_2O_3	Et_3SiSH	100[a]
28	CH_3SH	5% Pd-Al_2O_3	No reaction	...

[a] Not isolated; see Experimental Section.

reaction of a chlorosilane or siloxane with anhydrous or aqueous hydrogen fluoride. The only method we are aware of for conversion of a silicon–hydrogen bond to a fluorosilane is a transformation involving AgF or SbF_5.[8] It should be emphasized that this reaction with HF (and HCl) is fast and convenient and does not yield any side products, at least when the organo groups are alkyl or phenyl.

The reaction of HCl with the less hindered triethylsilane allowed a comparison of catalyst reactivities. As in the case of water,[9] palladium is the most effective catalyst. Reaction with HCl seemed to proceed as fast as the gas could be dissolved. The other catalysts were less efficacious, from 5% Rh–C, which took 34 min, to over 4.5 hr for 5% Pt–C, with 5% Ru–C (4 hr) being intermediate. This is slightly different from the hydrolysis reaction,[9] where the order seems to be Pd $\gg$ Ru $>$ Rh $\approx$ Pt. It is not clear why catalyst effectiveness is different in these cases.

Catalysis also offers a new route to relatively unhindered organosilylthiols. Other methods[10] generally involve cleavage of silicon–halogen or silicon–nitrogen bonds with H_2S or a metal hydrosulfide (*e.g.*, LiSH). However, reaction of H_2S with a chlorosilane can lead to disilthiane formation[10] and a hydrogen chloride acceptor is necessary. However, in the metal-catalyzed reaction, hindered silanes do not react readily (*e.g.*, reactions 18–20), probably because they cannot compete with H_2S for active catalyst sites, so that in effect the catalyst is poisoned. The less hindered silanes such as Et_3SiH can compete with H_2S and the reaction goes to completion. Failure of methanethiol to react may reflect its ability to poison the catalyst very effectively or may result from an extreme sensitivity of reaction rate to structural changes in the sulfur-containing reactant.

To test further the versatility of this synthetic method, a reaction was run on phenylmethylchlorosilane. It is known that halogenation of silicon–hydrogen bonds with halogen gets more difficult as more halogens are placed on the silicon, since one can stop at any stage with polyhydrosilanes.[6] This same effect was observed in the catalytic reaction, since, even after standing several hours in the presence of palladium catalyst and HCl, a substantial amount of phenylmethylchlorosilane was recovered, along with the expected phenylmethyldichlorosilane. Thus, it might also be possible to realize stepwise halogenation with the catalytic method.

Experimental Section

Solvents were dried by conventional methods and liquid amines were distilled from KOH prior to use. Gases were obtained from the Matheson Co. Catalysts were purchased from the following sources: 5% Pd-Al_2O_3, 5% Pd–C, 5% Ru–C, 5% Rh–C, and 5% Rh-Al_2O_3, Engelhard Industries, Inc.; 10% Pd–C, 5% Pt–C, chloroplatinic acid, Matheson Coleman and Bell; No. 28 Raney active nickel catalyst in water, Raney Catalyst Division, W. R. Grace and Co. The water was removed under vacuum from the last catalyst and it was stored under *p*-xylene. All starting materials and products were identified by comparative infrared spectra. When spectra were not available, absorption bands

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[8] H. H. Anderson, *J. Am. Chem. Soc.*, **80**, 5083 (1958).

[9] G. H. Barnes and N. E. Daugenbaugh, *J. Org. Chem.*, **31**, 885 (1966).

[10] Reference 6, Chapter 10.

were interpreted from known assignments.[11] References to compounds in the R_3Si^*- system are given.[12]

Procedure for Reactions 1-11.—A generalized procedure is as follows. In a 10-ml erlenmeyer flask was placed 0.5–0.6 g of R_3Si^*H which was dissolved in 5 ml of *p*-xylene. To this was added 50–60 mg of catalyst and then 0.25 ml of the amine. As soon as bubbles started appearing, the mixture was stirred and heated to 50–60°. After bubbling had ceased, the solution was cooled and filtered, and the solvent stripped. A rotation and an infrared spectrum were then taken. Results will be found in Table I.

Procedure for Reaction 12.—To 15.0 g of (−)-R_3Si^*H and 50 ml of xylene was added 1.50 g of 5% Pd–Al_2O_3. Methylamine was then bubbled in for 40 min and after an additional 10 min bubbles were rising from the catalyst. The reaction was then stirred for 16 hr, at the end of which time no bubbles were coming from the catalyst. After filtration and removal of solvent under vacuum, a rotation of the crude material (whose infrared spectrum indicated it to be pure $R_3Si^*NHCH_3$) was taken, $[\alpha]_D$ −2.7° (*c* 1.6, cyclohexane). After one crystallization from pentane, the yield was 9.7 g.

Procedure for Reactions 13 and 14.—The procedure is essentially the same as for hydrogen chloride. However, both catalysts seemed to form large clumps and the reaction took longer. For 10% Pd–C, it was 11 min until completion.

Procedure for Reactions 15–17.—In a 10-ml erlenmeyer flask a solution of 0.5–0.6 g of R_3Si^*H in *p*-xylene was prepared. To this was added 50–60 mg of catalyst and then HCl was bubbled in until the reaction stopped, usually about 5 min. The catalyst was then filtered, the solvent stripped, and a rotation taken. Results are found in Table I.

Procedure for Reactions 18 and 19.—To 0.51 g of R_3Si^*H in a 10-ml erlenmeyer flask was added 6 ml of CH_2Cl_2. Catalyst (60 mg) was added and then H_2S was bubbled in through a 10-mm glass frit. Almost immediately, bubbles arose from the catalyst, but the rate of bubbling decreased rapidly. After 6 hr there was no evidence of further reaction; so the mixture was filtered and the solvent stripped. The residue (which was mostly R_3Si^*H) was dissolved in 25 ml of pentane and 0.25 ml of diethylamine was added. The precipitate which formed, diethylammonium (α-naphthylphenylmethylsilyl)mercaptide, was removed by filtration and a rotation was taken in benzene. Data are in Table I.

Procedure for Reaction 21.—To a mixture of 0.12 g of 5% Pd–C and 25 ml of benzene in a 25-ml polyethylene flask was added 15 ml of Et_3SiH: bp 109°; $n^{21}{}_D$ 1.4109, lit.[13] $n^{20}{}_D$ 1.4117. Hydrogen fluoride was then bubbled in at the approximate rate of 2 bubbles/sec. There was an immediate vigorous evolution of gas and the reaction mixture became warm. Gas evolution slowed after 30 min and after 1 hr total time, stopped altogether. The mixture was filtered and distilled on a spinning-band column giving 9.8 g (78%) of Et_3SiF: bp 90–111° (the bulk at 110–111°); $n^{21}{}_D$ 1.3903 (lit.[13] $n^{20}{}_D$ 1.3900).

Procedure for Reaction 22.—To a mixture of 25 ml of benzene, 0.11 g of 5% Pd–C, and 15 ml of Et_3SiH was added hydrogen chloride. Gas was immediately evolved in copious amounts and the reaction was cooled in a water bath, owing to its exothermicity. Occasional swirling seemed to accelerate the reaction, which ended abruptly after 30 min. The mixture was filtered under nitrogen and the filtrate distilled on a spinning-band column, giving 12.0 g (85% yield) of Et_3SiCl: bp 90–147° (the bulk at 146–147°); $n^{21}{}_D$ 1.4309 (lit.[13] $n^{20}{}_D$ 1.4320).

Procedure for Reactions 23–28.—To a mixture of 50–60 mg of the appropriate catalyst, 15 ml of CH_2Cl_2, and 1 ml of Et_3SiH the proper gas was added for 1 min. Reactions 25 and 27 had no induction period, while for 23 it was 1 min and for 24, 11 min. In the case of reaction 26, the catalyst turned black, but there was no reaction. During the other reactions, gas was evolved and more reactant was added from time to time. After standing overnight to allow the catalyst to settle, infrared spectra were taken of the solutions, the Si–Cl stretch at 21.3 μ identifying the chlorosilanes[11] and the S–H stretch at 3.9 μ and the Si–S stretch at 21.8 μ confirming the identity of the triethylsilanethiol.[11]

Reaction of Phenylmethylchlorosilane with HCl.—To a mixture of 25 ml of benzene and 0.11 g of 5% Pd–C was added 15 ml of PhMeSiClH (Dow-Corning Corp., redistilled, bp 171–180°). There was a slight gas evolution, probably owing to reaction with HCl from hydrolysis of the chlorosilane. Hydrogen chloride was added and reaction was immediate and exothermic, but not so fast as with triethylsilane. Hydrogen chloride was added for 1.2 hr, at which time the reaction was very slow. After another 1.5 hr, the mixture was filtered under nitrogen and the filtrate distilled on a spinning-band column. The first silicon-containing fractions were 2.6 g of PhMeSiClH, bp 140–185°, and the next was phenylmethyldichlorosilane, bp 185–203° (the bulk at 200–203°) (lit.[13] bp 203–204°). The yield, 10.4 g (65%), allowing for recovered starting material, was identified by infrared spectrum, with the $SiCl_2$ stretching absorptions occurring at 18.1 and 19.8 μ.[11]

Registry No.—Hydrogen sulfide, 7783-06-4; (+)-R_3Si^*Pyr, 1041-96-9; (+)-R_3Si^*NHBu, 13192-32-0; (±)-R_3Si^*NHBu, 13221-16-4; (+)-$R_3Si^*NHCH_3$, 3554-00-5; (+)-R_3Si^*F, 13132-41-7; (+)-R_3Si^*Cl, 13132-42-8; (+)-$R_3Si^*S^-\ {}^+H_2NEt_2$, 13132-43-9.

Acknowledgment.—We thank Dow-Corning Corp. for continued generous support.

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[11] A. L. Smith, *Spectrochim. Acta*, **16**, 87 (1960); **19**, 849 (1963).

[12] R_3Si^*H, R_3Si^*Cl, and R_3Si^*F, ref 4; R_3Si^*NHBu and R_3Si^*Pyr, L. H. Sommer, J. D. Citron, and C. L. Frye, *J. Am. Chem. Soc.*, **86**, 5684 (1964); $R_3Si^*NHCH_3$, K. Ruhlmann, K. D. Kaufmann, and U. Mann, *Z. Chem.*, **5**, 107 (1965); $R_3Si^*S^-\ {}^+H_2NEt_2$, L. H. Sommer and J. McLick, *J. Am. Chem. Soc.*, **88**, 5359 (1966).

[13] Reference 5, Vol. II, part 1.