tion, for which there is much precedent, and electrophilic attack on carbon with *retention* of configuration, which also has much precedent. A possible alternative to operation of (b) and (c) in hydrosilation is direct conversion of intermediate I to product *via* essentially concerted addition of Si* and H to olefin in a *cis* manner. However, intermediate II is almost certainly involved in olefin isomerization.

The important and interesting question concerning whether Pt–C in the present work is really functioning as a heterogeneous catalyst for hydrosilation, or whether traces of Pt(II) or Pt(IV) on its surface comprise the real catalyst and are extracted by the reaction medium, is not answered by the demonstration of highly stereospecific retention of configuration for R_3Si^*H addition to 1-octene. Stereospecific replacement reactions of R_3Si^*H using group VIII metal catalysts such as Raney nickel in *heterogeneous* reactions have been found to proceed with *inversion* of configuration.[12] Thus, high stereospecificity at asymmetric silicon does not prove homogeneous catalysis, and the finding of a *retention* stereochemistry for R_3Si^*H in hydrosilation is not a trivial one.

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

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Stereospecific Substitution Reactions of Optically Active R_3Si^*H Catalyzed by Palladium and Nickel[1]

Sir:

It has long been known that the group VIII metals and metal halides catalyze the reaction of an organosilicon hydride with compounds containing the hydroxyl function.[2a–c]

$$R_3SiH + ZOH \xrightarrow{M} R_3SiOZ + H_2 \qquad (1)$$
$$Z = \text{H, alkyl, aryl, acyl, etc.}$$

Although reactions 1 provide a convenient method for the preparation of silanols,[3] alkoxy- (or aryloxy-) silanes,[4a–g] and silyl esters,[5a–d] and the synthetic scope has been greatly widened in recent years, information concerning the mechanism of the reaction has not been available.

The discovery that hydrosilation of 1-octene with optically active α-naphthylphenylmethylsilane, R_3Si^*H, proceeds with *retention* of configuration[6] led us to investigate the stereochemical course of reactions 1 using optically active organosilicon hydrides. Because of the profound effect that the metal surface may exert on the geometry of reaction, stereochemical data can play a powerful role in attempts to determine mechanisms of heterogeneous catalysis.[7] Indeed, the high reactivity of the silicon–hydrogen bond in such reactions and the availability of R_3Si^*H make stereochemical studies of reactions such as (1) seem especially worthwhile.

We wish to report that reactions 1 carried out with 10% palladium on carbon and Raney nickel catalysts[8] are highly stereospecific and proceed with *inversion* of configuration at the silicon center. Results are reported in Tables I and II. Except for R_3Si^*OPh,[9] correlations of configuration between R_3Si^*H and the other products have been reported previously.[10a–c]

The desired catalyst, 0.06 g, was mixed with a solution of 0.62 g of optically active R_3Si^*H in 6 ml of the designated solvent. An equimolar amount of the reagent was added and the reaction was allowed to proceed at room temperature in an atmosphere of dry nitrogen. After evolution of hydrogen had ceased, products were isolated in good yields and identified by comparison of infrared spectra with those of authentic samples.[9,10] With both catalysts, methanol was the most reactive, requiring 1–3 hr for complete reaction, and benzoic acid was the least reactive, requiring 2–4 days for complete reaction. Stereospecificity is gener-

Table I. Palladium-Catalyzed[a] Substitution Reactions of $(-)$-R_3Si^*H[b]

Reactant	Solvent	Product	Yield, %	$[\alpha]_D$[c]	Stereo-specificity[d]
Water	CH_2Cl_2	$(+)$-R_3Si^*OH	91	+12	81% invn
Methanol	*p*-Xylene	$(+)$-$R_3Si^*OCH_3$	95	+16	97% invn
Cyclohexanol	CH_2Cl_2	$(-)$-$R_3Si^*OC_6H_{11}$	89	−6.7	93% invn
Cyclohexanol	*p*-Xylene[e]	$(-)$-$R_3Si^*OC_6H_{11}$	86	−3.9	75% invn
t-Butyl alcohol	CH_2Cl_2	$(-)$-$R_3Si^*OC(CH_3)_3$	86	−11	70% invn
Phenol	CH_2Cl_2	$(+)$-R_3Si^*OPh	92	+2	63% invn[f]
Acetic acid	CH_2Cl_2	$(+)$-$R_3Si^*OOCCH_3$	79	+10	79% invn
Benzoic acid	CH_2Cl_2	$(+)$-R_3Si^*OOCPh	85	+11	80% invn

[a] 10% Pd–C; Matheson Coleman and Bell. [b] The $[\alpha]_D$ of the $(-)$-R_3Si^*H used was −33.6°. [c] Rotations (in degrees) taken in the solvent as reported in the literature.[10a–d] [d] A stereospecificity of 90%, for example, corresponds to a product which is 80% optically pure (20% racemic). Since the $(-)$-R_3Si^*H used in this reaction series was not optically pure, these values are adjusted correspondingly. [e] Reaction mixture was heated at 80° for 1.5 hr. [f] Based on a value of $[\alpha]_D$ +9.5° for optically pure R_3Si^*OPh, from unpublished results of R. Mason.

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(1) Support of this work by a grant from the National Science Foundation, GP-5662, is gratefully acknowledged.

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(3) G. H. Barnes and N. E. Daughenbaugh, *J. Org. Chem.*, **31**, 885 (1966).

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(8) In contrast to hydrosilation, we have found that platinum on carbon is not an effective catalyst for reaction of R_3Si^*H with substances containing the hydroxyl group. High temperatures are required and low yields are obtained. Chloroplatinic acid and platinous ethylene chloride catalyze reactions 1, but the products are racemic.

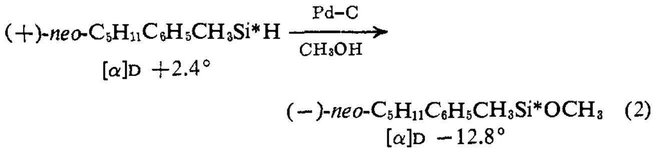
Table II. Raney Nickel[a] Catalyzed Substitution Reactions of (+)-R_3Si^*H[b]

Reactant	Solvent	Product	Yield, %	$[\alpha]_D$[c]	Stereospecificity[d]
Water	CH_2Cl_2	(−)-R_3Si^*OH	97	−17	94% invn
Methanol	*p*-Xylene	(−)-$R_3Si^*OCH_3$	94	−16.6	99% invn
Cyclohexanol	CH_2Cl_2	(+)-$R_3Si^*OC_6H_{11}$	98	+7.1	95% invn
Cyclohexanol	*p*-Xylene	(+)-$R_3Si^*OC_6H_{11}$	95	+7.9	99% invn
t-Butyl alcohol	CH_2Cl_2	(+)-$R_3Si^*OC(CH_3)_3$	91	+21	88% invn
t-Butyl alcohol	*p*-Xylene	(+)-$R_3Si^*OC(CH_3)_3$	93	+22	90% invn
Phenol	CH_2Cl_2	(−)-R_3Si^*OPh	97	−8.7	92% invn
Acetic acid	CH_2Cl_2	(−)-$R_3Si^*OOCCH_3$	84	−12	83% invn
Benzoic acid	CH_2Cl_2	(−)-R_3Si^*OOCPh	85	−12	83% invn

[a] No. 28 Raney Active Nickel Catalyst in Water, Raney Catalyst Division, W. R. Grace & Co. (water removed at reduced pressure and stored under xylene). [b] The α-NpPhMeSi*H used for this series was optically pure. [c] Rotation (in degrees) taken in the solvent as reported in the literature.[10a–d] [d] A stereospecificity of 90%, for example, refers to a product which is 80% optically pure (20% racemic). [e] Based on a value of $[\alpha]_D$ +9.5° for optically pure R_3Si^*OPh from unpublished results of R. Mason.

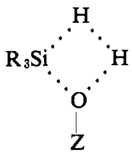
ally better with nickel than with palladium on carbon, and reaction rates are not greatly different.

The stereochemical paths of reactions 1 are not altered by a change in the structure of R_3SiH. Thus, when optically active neopentylphenylmethylsilane was treated with methanol in xylene using 10% palladium on carbon, the product[11] was formed with 98% inversion of configuration.



$$\underset{[\alpha]_D\ +2.4^\circ}{(+)\text{-}neo\text{-}C_5H_{11}C_6H_5CH_3Si^*H} \xrightarrow[CH_3OH]{Pd\text{-}C} \underset{[\alpha]_D\ -12.8^\circ}{(-)\text{-}neo\text{-}C_5H_{11}C_6H_5CH_3Si^*OCH_3} \quad (2)$$

Although a four-center mechanism such as (3) with the catalyst surface activating the silicon–hydrogen bond and perhaps also the oxygen–hydrogen bond would appear to be very attractive for reactions 1, on the basis of its simplicity, the present finding of *inversion* shows that the mechanism is more complex.[12]



(3)

It is interesting to note that certain hydrogenolysis reactions at asymmetric carbon centers proceed with inversion of configuration in the presence of heterogeneous catalysts.[13a–e] However, reactions involving cleavage of the carbon–hydrogen bond on the surface of group VIII metals generally lead to racemic products.[7,14] Our results show that reactions 1 lead to optically active products and are highly stereospecific.

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(9) Unpublished work of L. H. Sommer and R. Mason.

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The Oxymercuration–Demercuration of Representative Olefins. A Convenient, Mild Procedure for the Markovnikov Hydration of the Carbon–Carbon Double Bond

Sir:

The hydroboration–oxidation of olefins provides a highly convenient procedure for the anti-Markovnikov hydration of carbon–carbon double bonds.[1] The oxymercuration reaction,[2] combined with reduction of the oxymercurial intermediate by sodium borohydride[3] *in situ*, provides an equally convenient mild method to achieve the Markovnikov hydration of carbon–carbon double bonds without observable rearrangement.

The procedure is remarkable in its simplicity and speed. In a small flask, fitted with a magnetic stirrer, is placed 3.19 g (10.0 mmoles) of mercuric acetate. To this flask is added 10.0 cc of water, followed by 10.0 cc of tetrahydrofuran. Then 10.0 mmoles of 1-hexene is added. The reaction mixture is stirred for 10 min (at room temperature, approximately 25°) to complete the oxymercuration stage. Then 10.0 cc of 3 *M* sodium hydroxide is added, followed by 10.0 cc of a solution of 0.5 *M* sodium borohydride in 3.0 *M* sodium hydroxide. Reduction of the oxymercurial is almost instantaneous. The mercury is allowed to settle. Sodium chloride is added to saturate the water layer. The upper layer of tetrahydrofuran is separated—it contains an essentially quantitative yield of 2-hexanol (96%).

This simple procedure appears to be broadly appli-

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(1) G. Zweifel and H. C. Brown, *Org. Reactions*, **13**, 1 (1963).

(2) There is an enormous literature on the oxymercuration reaction, most of it concerned with the mechanism of the reaction, the stereochemistry of the products, and similar questions of primarily theoretical interest. For reviews with pertinent literature references, see J. Chatt, *Chem. Rev.*, **48**, 7 (1951), and N. S. Zefirov, *Russ. Chem. Rev.*, **34**, 527 (1965).

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