reported previously,[27] together with evidence for a chlorine atom transfer mechanism possibly concerted

$$t\text{-BuOCl} + \text{RC}{=}\text{CR} \longrightarrow t\text{-BuO}\cdot + \text{RCCl}{=}\dot{\text{C}}\text{R} \qquad (6)$$

with addition of the *t*-butoxy radical to another molecule of acetylene. A comparable termolecular process involving C–H bond cleavage is energetically feasible here, *e.g.*

$$2t\text{-BuOCl} + \text{RCHO} \longrightarrow 2t\text{-BuO}\cdot + \text{HCl} + \text{RCOCl} \qquad (7)$$

and "charge transfer" structures can easily be drawn as contributing to stabilization of the transition state. However, this provides strictly an *ad hoc* explanation, and the problem of such spontaneous initiation processes invites further study.[28]

Experimental Section

Reagents. Solvents and reactants either were commercial materials or were prepared by well-established methods. Physical constants were checked and, in general, purity confirmed by gas–liquid partition chromatography (glpc).

Competitive experiments were carried out as in previous papers in this series,[3] using small sample in sealed, degassed tubes and irradiating in a 0° thermostat with an incandescent lamp. Benzene, chlorobenzene, or *o*-dichlorobenzene were used as diluents to avoid rapid spontaneous reaction. Relative reactivities were calculated from disappearance of substrate (or, in some cases, appearance of products) by glpc analysis *vs.* internal standards with calibration as required. Comparisons were always between substrates of similar reactivity (preferably within a factor of 4), and referred back to standard (toluene or cyclohexane) in a stepwise manner. Since the whole sequence involved some 86 comparisons (all in duplicate to quadruplicate) individual experiments are not listed, but only experimental uncertainties (mean deviations) using standard formulas for the propagation of errors. Calculation of relative reactivities for *t*-butyl alcohol and acetone were corrected for the fact that they are produced as well as being consumed during the reaction.

Products were determined from reactions run either in sealed tubes or small flasks. Since α-chloro ethers are highly unstable, they were usually identified by hydrolysis to the carbonyl compound and comparison of derivatives with authentic materials. Acid chlorides were similarly converted to methyl esters. Other products were separated by glpc, collected, and identified by infrared spectra or other physical properties. In ether halogenations leading to β scission, the amount of alkyl chloride produced was used as the measure of the β-scission process.

Halogenation of Ketones. *t*-Butyl hypochlorite reacts rapidly with acetone in the dark in the presence of trifluoroacetic acid (1:10:0.1) to give chloroacetone and *t*-butyl alcohol in almost quantitative yield in less than 3 hr. Similarly, cyclopentanone (2 ml), hypochlorite (0.5 ml), and acetic acid (5 ml) give 2-chlorocyclopentanone quantitatively in less than 1.5 hr. Degassed solutions of hypochlorite in cyclopentanone are stable in the dark at 0° but react on irradiation. Glpc analysis yielded 2-chlorocyclopentanone and cyclopenten-3-one. The unsaturated ketone was assumed to come from 3-chlorocyclopentanone, since it was not present in the reaction mixture and since the 2-chloro ketone is stable under the analysis conditions. With 3-pentanone, both chloro products were stable and could be isolated.

The ratio of products from cyclopentanone remained constant when treated as described, in the presence of $NaHCO_3$, pyridine, or in refluxing Freon 11 to sweep out any HCl formed. Accordingly we conclude that they arise solely from the radical process.

Spontaneous Initiation Experiments. *t*-Butyl hypochlorite (0.7 ml) was added to a mixture of 1 ml each of freshly distilled benzaldehyde, cyclohexane, and 2,3-dimethylbutane at 0° under a N_2 atmosphere. After 1 hr the residual hypochlorite was destroyed with H_2O–KI and the organic layer analyzed by glpc for cyclohexyl chloride and the two chloro-2,3-dimethylhexanes. Because of the high reactivity of benzaldehyde, only very small quantities of the chlorides were present (about 4% total yield). Relative yields were cyclohexyl chloride 68%, 2-chloro-2,3-dimethylbutane 29%, and 1-chloro-2,3-dimethylbutane 3%. A similar experiment using diethyl ether in place of benzaldehyde gave 61.37 and 2%, respectively, but an even lower total yield. Both results agree, within experimental uncertainty because of the low yields, with photoinitiated reactions in the absence of aldehyde or ether (61, 36, and 3%, respectively).

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(27) C. Walling, L. Heaton, and D. D. Tanner, *J. Am. Chem. Soc.*, **87**, 1715 (1965).

(28) In particular, spontaneous processes involving molecular chlorine occur with olefins (where hypochlorite is stable) but not with acetylenes or ethers; *cf.* M. Poutsma, *ibid.*, **87**, 2161, 2172 (1965).

Communications to the Editor

Stereochemistry of Asymmetric Silicon. Stereospecific Platinum-Catalyzed Hydrosilation of 1-Octene with Optically Active R_3Si^*H[1,2]

Sir:

The first example of hydrosilation, addition of a silicon hydride to an olefin, involved reaction of trichlorosilane with 1-octene in the presence of diacetyl peroxide and was reported in 1947.[3] During the next two decades hydrosilation became an exceedingly important laboratory and industrial process, and it was discovered that platinum–charcoal and chloroplatinic acid are very effective catalysts.[4]

$$\equiv\text{SiH} + \text{CH}_2{=}\text{CH—R} \xrightarrow[\text{H}_2\text{PtCl}_6]{\text{Pt–C} \atop \text{or}} \equiv\text{SiCH}_2\text{CH}_2\text{R} \qquad (1)$$

Beginning with the observation that primary alkylsilanes often result from reactions involving nonterminal olefins, as in reaction 2,[5] Speier and co-workers

$$\text{Cl}_2(\text{CH}_3)\text{SiH} + \text{CH}_3\text{CH}{=}\text{CHCH}_2\text{CH}_3 \xrightarrow{\text{H}_2\text{PtCl}_6} \text{CH}_3(\text{CH}_2)_3\text{CH}_2\text{Si}(\text{CH}_3)\text{Cl}_2 \qquad (2)$$

have engaged in an intensive study of the mechanism of reactions 1.[6] This work revealed that platinum-catalyzed hydrosilation is often accompanied by olefin isomerization which is significantly altered by the presence of silane,[6a–c] and that hydrosilation carried out with Cl_3SiD results in extensive exchange between Si–D and C–H of the olefin plus the formation of adducts having deuterium widely distributed in their structures, as in reaction 3.[6c]

$$3.56\text{Cl}_3\text{SiD} + \text{CH}_2{=}\text{C}(\text{CH}_3)_2 \xrightarrow{\text{H}_2\text{PtCl}_6} \text{Cl}_3\text{SiC}_4\text{H}_{6.5}\text{D}_{2.5} + 1.5\text{Cl}_3\text{SiH} + \text{Cl}_3\text{SiD} \qquad (3)$$

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(1) In its initial stages this work was supported by a grant from the Dow Corning Corporation. Later work was supported by Grant GP-5662 from the National Science Foundation.

(2) Work carried out in part at The Pennsylvania State University.

(3) L. H. Sommer, E. W. Pietrusza, and F. C. Whitmore, *J. Am. Chem. Soc.*, **69**, 188 (1947).

(4) For an excellent review up to about 1959, see C. Eaborn, "Organosilicon Compounds," Academic Press Inc., New York, N. Y., 1960, pp 45–64.

(5) J. L. Speier, J. A. Webster, and G. H. Barnes, *J. Am. Chem. Soc.*, **79**, 974 (1957).

(6) (a) J. L. Speier and J. C. Saam, *ibid.*, **80**, 4104 (1958); (b) *ibid.*, **83**, 1351 (1961); (c) J. W. Ryan and J. L. Speier, *ibid.*, **86**, 895 (1964); (d) M. C. Musolf and J. L. Speier, *J. Org. Chem.*, **29**, 2519 (1964); (e) J. W. Ryan and J. L. Speier, *ibid.*, **31**, 2698 (1966).

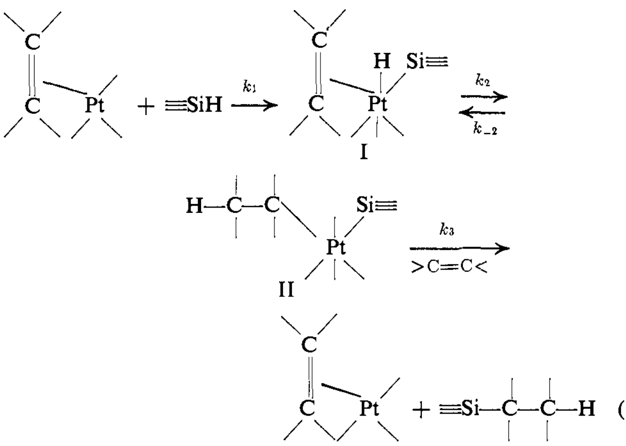
Table I. Hydrosilation of 1-Octene with (+)-R_3Si^*H[a]

No.[b]	Catalyst	Reaction temp, °C	Reaction time	$[\alpha]_D$, deg, of product	Yield, %	Stereochemistry[d,e]
1[c]	Pt–C	130–140	24 hr	−1.8	85	100% retn
2	$H_2PtCl_6 \cdot 6H_2O$	130–140	24 hr	−1.8	75	100% retn
3	$H_2PtCl_6 \cdot 6H_2O$	~25	2 weeks	−1.7	61	97% retn
4	Pt(II)–olefin	130–140	65 hr	−1.5	56	92% retn
5	Pt(II)–olefin	~25	2 weeks	−1.4	27	89% retn

[a] The α-naphthylphenylmethylsilane reactant had $[\alpha]_D$ +34.6°. [b] Runs 1, 2, and 4 used a 1:2 molar ratio of silane to olefin, 5 g of R_3Si^*H, and 10 mg of catalyst for each run. Runs 3 and 5 used a 1:4 molar ratio of silane to olefin, 3 g of R_3Si^*H, 10 mg of catalyst for 3, and 20 mg of catalyst for 5. [c] The room temperature Pt–C reaction is very slow relative to runs 3 and 5. [d] A stereochemistry of, say, 90% retention means that the product was 80% optically pure. [e] R_3Si^*-n-C_8H_{17} having $[\alpha]_D$ 1.8° is assumed to be optically pure, based on previous studies which have shown that R_3Si^*Cl and RLi give products of high optical purity.[8]

In a significant extension of the above studies, Chalk and Harrod[7] have reported that a Pt(II)–olefin complex, $((C_2H_4)PtCl_2)_2$, provides homogeneous catalysis of hydrosilation and concurrent olefin isomerization, and that the presence of silane markedly affects the olefin isomerization profile. It was also found[7] that the Pt(II)–olefin catalyst gave results very similar to those obtained with chloroplatinic acid. In addition, it was reported that a phosphine complex of iridium(I) cleaved a variety of silicon hydrides, retaining both the hydride and silicon fragments in the iridium coordination sphere.

On the basis of the above results, both research groups[6c,7] have concluded that hydrosilation catalyzed by chloroplatinic acid or Pt(II)–olefin involves an intermediate in which silicon and alkyl are both bonded to a platinum center, and that such intermediates may form adducts or revert to olefin which may be isomerized. The detailed mechanism advanced for catalysis by Pt(II)–olefin is as follows.[7]



(4)

We wish to report that addition to 1-octene of an optically active silane, α-naphthylphenylmethylsilane, R_3Si^*H, proceeds with a high degree of stereospecificity with three catalyst systems: 5% Pt–C, chloroplatinic acid, and $((C_2H_4)PtCl_2)_2$. Furthermore, as indicated in Table I, *all three catalysts give retention of configuration at the asymmetric silicon center.*

In view of previously assigned stereochemical paths for formation of R_3Si^*Cl from R_3Si^*H and for coupling of R_3Si^*Cl with RLi reagents,[8] the stereochemical sequence given below shows that (+)-R_3Si^*H and (−)-R_3Si^*-n-C_8H_{17} have the same configuration.

$$\begin{array}{ccccc} (+)\text{-}R_3Si^*H & \xrightarrow[\text{retn}]{Cl_2} & (-)\text{-}R_3Si^*Cl & \xrightarrow[\text{invn}]{n\text{-}C_8H_{17}Li} & (+)\text{-}R_3Si^*\text{-}n\text{-}C_8H_{17} \\ [\alpha]_D\ +34.6^\circ & & [\alpha]_D\ -6.3^\circ & & [\alpha]_D\ +1.8^\circ \end{array}$$

The infrared spectrum and elemental analysis (*Anal.* Found: Si, 7.86; C, 83.5; H, 9.1) of R_3Si^*-n-C_8H_{17} were completely consistent with the assigned structure, and the infrared spectra of the hydrosilation products were identical with that of the authentic substance.

The finding of a highly stereospecific retention stereochemistry for asymmetric silicon in hydrosilation has some interesting mechanistic implications. For example, free silyl radicals or ions are clearly not involved, and the cleavage of the Si–H bond by the metal center must proceed with virtually pure retention of configuration. Furthermore, the transfer of asymmetric silicon from the metal center to olefinic carbon must also proceed with virtually pure retention of configuration.

There is a further stereochemical aspect of hydrosilation which has been explored previously. In a series of elegant studies, Benkeser and co-workers found that addition of Cl_3SiH to 1-alkynes in the presence of Pt–C or chloroplatinic acid proceeded in a *cis* manner to form *trans*-1-trichlorosilyl-1-alkenes.[9] Also, reaction of a large excess of Cl_3SiH with 1-methyl-d_3-cyclohexene in the presence of chloroplatinic acid gave *cis* addition to the ring.[10] More recently, it has been found[4e] that addition of $MeHSiCl_2$ to 2-butyne in the presence of chloroplatinic acid proceeds in a *cis* manner with formation of *cis*-(2-methyldichlorosilyl)butene-2.

Retention of configuration at silicon and *cis* addition to olefin in hydrosilation are in harmony with mechanism sequence 4 if the following stereochemical processes are involved: (a) insertion of the platinum center into the silicon–hydrogen bond proceeds with *retention* of configuration at silicon; (b) conversion of intermediate I to II results in *cis* addition of hydrogen and platinum to the double bond; (c) product formation from II takes place with *retention* of configuration at both silicon and carbon.

Retention of configuration in process a is reasonable, and *cis* addition of D_2 to fumaric acid, catalyzed by Ru(II), has been postulated to involve a process analogous to (b).[11] Process c may be regarded as proceeding by a quasi-cyclic (SNi–Si) mechanism involving nucleophilic attack on silicon with *retention* of configura-

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[7] A. J. Chalk and J. F. Harrod, *J. Am. Chem. Soc.*, **87**, 16 (1965).

[8] L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill Book Co., New York, N. Y., 1965; L. H. Sommer, W. D. Korte, and P. G. Rodewald, *J. Am. Chem. Soc.*, **89**, 862 (1967).

[9] R. A. Benkeser and R. A. Hickner, *ibid.*, **80**, 5298 (1958); R. A. Benkeser, M. L. Burrous, L. E. Nelson, and J. V. Swisher, *ibid.*, **83**, 4385 (1961).

[10] T. G. Selin and R. West, *ibid.*, **84**, 1863 (1962).

[11] J. Halpern, J. F. Harrod, and B. R. James, *ibid.*, **88**, 5150 (1966). We are indebted to a referee for calling our attention to this reference and to the possibility of operation of process b.

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.

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

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Received December 29, 1966

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]

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

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, %	[α]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 [α]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 [α]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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(6) L. H. Sommer, *et al.*, *J. Am. Chem. Soc.*, **89**, 1519 (1967).

(7) *Cf.* R. L. Burwell, *Chem. Rev.*, **57**, 895 (1957).

(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.