temperature. The mixture resulting from quenching this solution with 75 ml of water was extracted with diethyl ether. The combined ether extracts were washed with water and saturated sodium chloride solution, dried, and taken to dryness under nitrogen. Evaporation of the ether solution under nitrogen provided 468 mg (100%) of 4-hydroxy[2.2]paracyclophane, mp 223–228° (sealed evacuated capillary) (lit.[3a] mp 225–229°). The nmr spectrum showed peaks centered at $\delta = 3.02$ ppm (bridging methylenes), $\delta = 4.45$ ppm (hydroxyl hydrogen), $\delta = 5.62$ ppm (orthohydrogen), and $\delta = 6.50$ ppm (rest of aromatic protons). Strong and medium peaks in the infrared spectrum were found at 3610 (CCl_4 solution), 2920, 1560, 1495, 1415, 1260, 1140, 1085, 975, 795, 715, 665, and 612 cm^{-1}.

pK_A Measurements.—A standard spectroscopic method[14] for determining pK_A values was used. Ultraviolet spectra were determined on solutions approximately 10^{-5} *M* in phenol or amine in 5% (w/w) methanol–water, using a 0–0.1-o.d. slide wire (Table II). The necessary pH determinations were made on a Radiometer pH meter, Model 4d, using a Type G-200B high pH electrode, on the 3-ml spectroscopic sample immediately after obtaining the ultraviolet spectrum. The analytical wavelength for the amine was 318 mμ, while for the phenol two wavelengths were used: 276 and 329.5 mμ.

TABLE II

ULTRAVIOLET SPECTRA

Compound	Solvent system	λ, mμ	Log ε
4-Hydroxy[2.2]paracyclophane	5% MeOH–H_2O[a]	224	4.172
		289	2.806
		310	2.748
4-Hydroxy[2.2]paracyclophane	95% EtOH[b]	224	4.17
		283	2.78
		290	2.87
		312	2.78
4-Hydroxy[2.2]paracyclophane, anion	5% MeOH–H_2O[a]	277	3.343
		329	1.136
4-Hydroxy[2.2]paracyclophane, anion	95% EtOH[b]	284	3.08
		332	2.75
4-Amino[2.2]paracyclophane,	5% MeOH–H_2O[a]	226	4.120
		270	3.314
		318	2.785
4-Amino[2.2]paracyclophane,	95% EtOH[b]	222	4.2
		272	3.41
		323	2.82
4-Amino[2.2]paracyclophane, cation	5% MeOH–H_2O[a]	223	4.238
		286	2.474
		307	2.143
4-Amino[2.2]paracyclophane, cation	95% EtOH[b]	223	4.26
		286	2.41
		303	2.13

[a] This work. [b] Reference 6.

From seven to nine different solutions were used for each determination. Typical Δo.d. values were 0.05 to 0.09. The pH meter was standardized against standard aqueous buffers between each reading. No correction was applied to meter readings for differences in the activity of acid or base in 5% methanol–water and water, since this correction would be small.[15] Solutions and cell compartments were at 25.0°. The pK_A of phenol, determined in this solvent, was 10.01 [lit.[16] (preferred values, 25°, in water, by eight investigators, using both potentiometric and spectroscopic methods) was 9.88 to 10.08].

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Test of the Reversibility of the Platinum-Catalyzed Hydrosilylation of Olefins

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The addition of silicon hydrides across unsaturated carbon–carbon bonds under the remarkably efficient catalysis by chloroplatinic acid and other platinum compounds has been extensively studied by Speier and co-workers,[2] as well as many others.[3] The tendency to form primary alkylsilanes from nonterminal olefins was observed,[2a,b,4] although other isomerizations have been noted.[5,6] The various recent mechanisms proposed[2b,4,7,8] have generally concurred that the terminal adduct observed does not arise from rearrangement of another adduct, but, instead, comes from isomerization of the olefin on the catalyst surface, either with or without the required presence of a hydrosilane, followed by the addition reaction.

The present report describes a test of whether or not there is a kinetically significant equilibrium involving the terminal addition compound and its precursors, the olefin, and the hydrosilane at temperatures up to 100° in the presence of homogeneous and heterogeneous platinum catalysts. For this purpose, an optically active alkyl substituent, (*S*)-2-methylbutyl, on silicon was selected since it contains only one asymmetric center, the β carbon, and this bears the requisite hydrogen atom. Moreover, suitable synthetic methods have already been developed for the necessary compounds.[9] If an equilibrium (eq 1) occurred with significant rate and physical separation of reactants, then racemization of the alkyl group should be observed.

$$\underset{\text{I}}{C_2H_5(CH_3)\text{–}C^*H\text{–}CH_2\text{–}SiX_3} \rightleftharpoons C_2H_5(CH_3)C{=}CH_2 + HSiX_3 \qquad \begin{matrix}\text{a, } X = H \\ \text{b, } X = Cl\end{matrix} \qquad (1)$$

Under platinum-catalyzed hydrosilylation conditions (see Table I) attempts were made to racemize both (+)-(*S*)-2-methylbutylsilane (Ia) and (+)-(*S*)-2-methylbutyltrichlorosilane (Ib). The experimental results are given in Table II. The observed optical rotation values taken before and after each of the various runs show some shifts both negative and positive. However, these are considered to be within experimental

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TABLE I

ADDITION OF TRICHLOROSILANE TO 2-METHYL-1-BUTENE

Reactants, mmoles[a]		Catalyst	Yield, %[b]
$HSiCl_3$	C_2H_5-(CH_3)-C=CH_2		
62	50	0.0664 g of 5% Pt–C	55.3
63	50	0.65 mmole of H_2PtCl_6	93.0
58	49	No catalyst	0.0

[a] Conditions: in sealed tube, 20 hr at 100°. [b] Product is racemic 2-methylbutyltrichlorosilane.

TABLE II

(+)-(S)-2-METHYLBUTYLSILANES IN THE PRESENCE OF HYDROSILYLATION CATALYSTS

Silane,[a] g	Catalyst, moles/mole of silane	Reacn conditions	$[\alpha]^{20}D$, deg	
			Before	After[d]
$RSiH_3$, 2.98	Pt,[b] 1.5 × 10^{-5}	20°, 96 hr	+9.68	+9.45
$RSiH_3$, 3.10	Pt,[b] 3.3 × 10^{-5}	75° (reflux), 20 hr	+9.68	+9.58
$RSiH_3$, 3.00	Pt,[b] 1.0 × 10^{-4}	100° (sealed tube), 20 hr	+9.58	+9.56
$RSiH_3$, 2.77	Pt,[c] 0.056 g	100° (sealed tube), 20 hr	+9.56	+9.52
$RSiCl_3$, 4.11	Pt,[b] 1.5 × 10^{-4}	100° (sealed tube), 24 hr	+11.45	+11.32
$RSiCl_3$, 5.15	Pt,[c] 0.063 g	100° (sealed tube), 24 hr	+11.32	+11.54

[a] R = (S)-2-Methylbutyl. [b] Catalyst is *ca.* 10^{-2} *M* $H_2PtCl_6 \cdot 6H_2O$ in isopropyl alcohol. [c] Catalyst is 5% platinum on powdered charcoal. Value in grams is actual weight. [d] Rotation of product silane isolated after reaction.

uncertainty and imply absence of significant racemization.

To provide a more stringent test, two additional types of experiments were conducted. In the first, the attempted racemizations were performed in the presence of more than equivalent molar quantities of 2-methyl-1-butene with the goal of competing with any possibly stereospecifically oriented olefin in a tight complex with a hydrosilane as the right-hand side of equilibrium 1. No racemization occurred. In the second set of runs, the active trichlorosilane (Ib) was present in equimolar quantities with 2-methyl-1-butene undergoing hydrosilylation with a 33% excess of trichlorosilane. The reaction went well and the mixture of original active and *in situ* generated inactive product, when isolated, displayed a rotation value consistent with nonracemization, if one accepts the reasonable assumption that asymmetric induction is not significant in this system. If it were it would have to counterbalance rather closely the degradation in activity due to racemization since the observed rotation agrees with that predicted if the active material behaved solely as a labeling component in the total product.

It appears then that, under a variety of dynamic conditions, an asymmetric hydrogen-bearing carbon atom in the β position to silicon does not racemize under hydrosilylation conditions. Hence, this latter reaction does not, at least for the primary alkylsilane case (*i.e.*, terminal silicon), involve a kinetically significant equilibrium between hydrosilylation products and their precursors.

Experimental Section

All inorganic reagents and solvents were obtained from Matheson Coleman and Bell, Inc. Trichlorosilane (bp 31–33°), chloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$), and 5% platinum on powdered charcoal were used without further purification. In the reactions, chloroplatinic acid was employed as a freshly prepared solution, approximately 10^{-2} *M*, in isopropyl alcohol. 2-Methyl-1-butene was distilled (bp 31–32°) prior to use. The optically active compounds, (+)-(S)-2-methylbutylsilane and (+)-(S)-2-methylbutyltrichlorosilane, were prepared as described elsewhere.[9]

The sealed tube experiments were performed in 18-mm-o.d. Pyrex glass tubing. A smaller bore tube, containing the catalyst was placed within the larger one charged with the other reactants. Under dry nitrogen purge, the system was chilled in liquid nitrogen and flame sealed, and the reactants were mixed by inversion. After the indicated reaction time, the tubes were again cooled in liquid nitrogen before being opened.

Optical rotation values were obtained on a Rudolph Model 80 polarimeter.

Addition of Trichlorosilane to 2-Methyl-1-butene.—Neat mixtures of trichlorosilane and 2-methyl-1-butene with 5% platinum–charcoal, chloroplatinic acid (in isopropyl alcohol), and no catalyst, respectively, were heated in sealed tubes at 100° for 20 hr. Specific experimental parameters and yields of product, isolated by distillation (bp 162–169°) are presented in Table I. In all cases, the product was optically inactive. It is evident that, for these conditions, silylation requires a catalyst, and that the homogeneous platinum catalyst used is better, in terms of yield, than is the heterogeneous one.

Attempted Racemization of (+)-(S)-2-Methylbutylsilane and (+)-(S)-2-Methylbutyltrichlorosilane.—Subject silanes were treated with chloroplatinic acid and platinum–charcoal under the conditions given in Table II. Post-reaction work-up involved isolation of the silanes by distillation and comparison of optical rotation values ($[\alpha]^{20}D$) with those of the initial reactants.

Attempted Racemization in the Presence of Excess Olefin.—(+)-(S)-2-Methylbutyltrichlorosilane (7.12 g, 35 mmoles), 2-methyl-1-butene (3.00 g, 43 mmoles), and chloroplatinic acid (0.06 ml of 1.05 × 10^{-2} *M* solution in isopropyl alcohol, corresponding to 2.1 × 10^{-5} mole/mole of butene) were heated in a sealed tube for 20 hr at 100°. The silane isolated by distillation had $[\alpha]^{20}D$ 11.46° compared to an initial value of 11.45°.

Attempted Racemization in the Presence of a Dynamic Hydrosilylation Reaction.—(+)-(S)-2-Methylbutyltrichlorosilane (6.13 g, 30 mmoles), trichlorosilane (5.50 g, 41 mmoles), 2-methyl-1-butene (2.15 g, 31 mmoles), and chloroplatinic acid (0.06 ml of 1.05 × 10^{-2} *M* solution, corresponding to 2.1 × 10^{-5} mole/mole of butene) were heated in a sealed tube for 20 hr at 100°. The silane isolated by distillation, 12.09 g (59 mmoles), represented 93.5% yield in the hydrosilylation reaction. The observed $[\alpha]^{20}D$ value for the mixture of active and inactive silane product isolated by distillation was 5.76°. That calculated, by assuming that the added active silane took no part in the reaction (was not racemized) and that the hydrosilylation addition gave 100% yield of inactive silane, was 5.61°.

The Use of Benzophenone N-Chlorimine and N-Bromimine as Halogenating Agents[1]

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In the course of a study of the *syn–anti* isomerization of substituted benzophenone N-chorimines and N-bromimines[3] it was found that halogenation of cyclohexane used as a solvent was occurring under certain

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[1] Taken from the Ph.D. Thesis of C. G. M., University of Illinois, 1963.

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