Vinyl- and Allylsilanes from the Rhodium(I)-Catalyzed Hydrosilylation of 1-Alkenes with Trialkylsilanes

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Introduction

The transition-metal-catalyzed hydrosilylation of C=C in 1-alkenes with trialkylsilanes runs into hundreds of references.[1] In most cases the corresponding 1-silyl-substituted alkanes were the sole products ($R_3SiCH_2CH_2R'$). With styrene a mixture of 1- and 2-silyl-substituted phenylethanes was usually obtained ($R_3SiCH_2CH_2Ph$ and $R_3SiCH(CH_3)Ph$). There are only a few isolated reports in the literature on the hydrosilylation of 1-alkenes that produce unsaturated products ($R_3SiCH{=}CHR'$),[2-5] although such compounds are readily prepared via hydrosilylation of 1-alkynes.[1] Recently, we reported on the Rh(I)-catalyzed hydrosilylation of styrene to give *trans*-$R_3SiCH{=}CHPh$ as the major product.[5] In this case the formation of unsaturated product was favored by the high Rh(I) concentration. Extending this work, we now report on the hydrosilylation of 1-alkenes in the Rh(I) system. The unsaturated product was found to consist not only of vinylsilanes but additionally of allylsilanes ($R_3SiCH_2CH{=}CHR'$).

Results

The reaction of methyldi-*n*-decylsilane with mixture, in the presence of Wilkinson's catalyst was carried out under the reported conditions[6] (80–85 °C, Rh(I)/R_3SiH, 2.3×10^{-4} mol/mol) to give methyldi-*n*-decyl-*n*-octylsilane (**1**) (90%). A small amount of product (~5%) later identified as 1-(methyldi-*n*-decylsilyl)-*trans*-1-octene (**2a**) was present as a shoulder of the GLC peak of the major product. The same two peaks were obtained in a 40:60 ratio when the amount of Rh(I) was increased tenfold (Table I). The peak representing the major product was identified by coinjection with an authentic sample of **1**.

$$CH_3(n\text{-}C_{10}H_{21})_2SiH + H_2C{=}CHC_6H_{13}\text{-}n \xrightarrow{\text{Rh(I)}} CH_3(n\text{-}C_{10}H_{21})_2Si(n\text{-}C_8H_{17}) + n\text{-}C_8H_{18} +$$
$$\mathbf{1}$$
$$CH_3(n\text{-}C_{10}H_{21})_2SiCH{=}CHC_6H_{13}\text{-}n +$$
$$\mathbf{2a}, \text{trans} \quad \mathbf{2b}, \text{cis}$$
$$CH_3(n\text{-}C_{10}H_{21})_2SiCH_2CH{=}CHC_5H_{11}\text{-}n$$
$$\mathbf{3a}, \text{trans} \quad \mathbf{3b}, \text{cis}$$

The infrared spectrum of the mixture however, showed unsaturation. On the basis of NMR (^1H, ^{13}C, and ^{29}Si), the products were identified as **1** (60%), **2a** (32%), 1-(methyldi-*n*-decylsilyl)-*trans*-2-octene (**3a**) (5%), and 1-(methyldi-*n*-decylsilyl)-*cis*-2-octene (**3b**) (3%). To aid characterization of the product, methyldi-*n*-decylsilane was reacted with 1-octyne by using chloroplatinic acid or Wilkinson's catalyst. With chloroplatinic acid, the largest hydrosilylation product was **2a** (80%).[7] Wilkinson's catalyst gave mostly a mixture of **2a** (44%) and **2b** (54%). Ruthenium carbonyl gave products analogous to chloroplatinic acid catalyst. Results are summarized in Table I, and diagnostic NMR data are given in Table II.

After the unreacted octenes were distilled, hydrogenation of the product mixture proceeded slowly to give **1**, which gave satisfactory elemental analysis and only a single peak in the ^{29}Si NMR spectrum of the product. The low reactivity of the mixture toward hydrogenation was attributed to the presence of hindered C=C bonds, which also required a homogeneous catalyst ($RhCl(PPh_3)_3$) to be successful. The recovered octene fraction above was partially isomerized.

Discussion

It was reported that the Rh(I)-catalyzed hydrosilylation of 1-alkenes with trialkylsilanes gave ~95% of the corresponding *n*-alkylsilane.[8] The remaining 5% of the product was attributed to isomeric alkylsilanes, but no evidence was presented to support this assumption. The authors[8] apparently based their assumption on the fact that recovered olefin was highly isomerized and that isomeric products have been known to form with chloroplatinic acid.[1] We found that the minor products as reported above were misassigned and are actually the unsaturated compounds, which can become dominant products of reaction when high concentrations of Rh(I) are used. The unsaturated products consisted predominantly of *trans*-vinylsilane **2a** and a mixture of *trans*- and *cis*-allylsilanes **3a** and **3b**, respectively. Haszeldine et al.[9] studied the reaction of 1-hexene with triethylsilane and observed an effect of [Rh(I)] on the rate of reaction and isomerization of 1-hexene, but the type of product formed apparently was assumed to be the same in all cases.

Since our work indicates that formation of unsaturated products can compete with the normal hydrosilylation reaction, it is appropriate to define the circumstances that favor one or the other type of reaction. For this study, we investigated the reaction of 1-decene with triethylsilane since all products in question were cleanly resolved by capillary GLC. In practice, **6b** was detected in some runs in small amounts.

$$Et_3SiH + H_2C{=}CHC_8H_{17}\text{-}n \xrightarrow{\text{Rh(I)}} Et_3SiC_{10}H_{21}\text{-}n + n\text{-}C_{10}H_{22} + Et_3SiCH{=}CHC_8H_{17}\text{-}n +$$
$$\mathbf{5} \qquad\qquad \mathbf{6a}, \text{trans}$$
$$\mathbf{6b}, \text{cis}$$
$$Et_3SiCH_2CH{=}CHC_7H_{15}\text{-}n$$
$$\mathbf{7a}, \text{trans}$$
$$\mathbf{7b}, \text{cis}$$

Products of Reaction. To establish the source of unsaturated products, triethylsilane was reacted with 1-decene under conditions shown in Table III (first entry), following the course of reaction by GLC. It was shown that both unsaturated compounds (vinylsilane **6a** and allylsilanes **7a** and **7b**) were present in the mixture at silane conversion of ~20% and that the ratio of **6a**/(**7a** + **7b**) remained constant (~1.9/1) for ~80% of the reaction.

(1) For the latest review of hydrosilylation reaction see: Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407.
(2) Seki, Y.; Takeshita, K.; Kawamoto, K.; Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 928.
(3) Marciniec, B.; Gulinski, J. *J. Organomet. Chem.* **1983**, *253*, 349.
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(5) Onopchenko, A.; Sabourin, E. T.; Beach, D. L. *J. Org. Chem.* **1983**, *48*, 5101.
(6) Rejhon, J.; Hetfleja, J. *Collect. Czech. Chem. Commun.* **1975**, *40*, 3680.
(7) Green, M.; Spencer, J. L.; Stone, G. G. A.; Tsipis, C. A. *J. Chem. Soc., Dalton Trans.* **1977**, 1519, 1525.
(8) Haszeldine, R. N.; Parish, R. V.; Parry, D. J. *J. Chem. Soc. A* **1969**, 683.
(9) Haszeldine, R. N.; Parish, R. V.; Taylor, R. J. *J. Chem. Soc., Dalton Trans.* **1974**, 2311.

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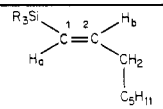
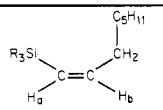
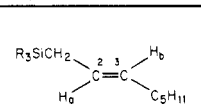
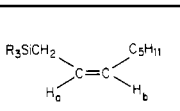
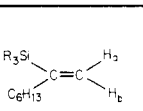
Table I. Hydrosilylation of 1-Octene and 1-Octyne with Methyldi-*n*-decylsilane (R_3SiH)

		products,[g] % molar selectivity						
		$R_3SiC_8H_{17}$	$R_3SiCH{=}CHC_6H_{13}$		$R_3SiCH_2CH{=}CHC_5H_{11}$		$R_3SiC(C_6H_{13}){=}CH_2$	
feed	cat.	1	2a (trans)	2b (cis)	3a (trans)	3b (cis)	4	n-C_8H_{18}[h]
1-octene	$RhCl(PPh_3)_3$[a]	60	32		5	3		38
	$Ru_3(CO)_{12}$[b]	11	47		32	11		87
	$H_2PtCl_6{\cdot}6H_2O$[c]	96						
1-octyne	$RhCl(PPh_3)_3$[d]		44	54			2	
	$Ru_3(CO)_{12}$[e]		71	15			14	
	$H_2PtCl_6{\cdot}6H_2O$[f]		80	10			10	

[a] R_3SiH, 4.7 mmol; 1-octene, 22.3 mmol; Rh/R_3SiH, 2.1×10^{-3} M; benzene, 5 mL; 70 °C, 2 h, N_2. R_3SiH conversion, 100%. [b] R_3SiH, 3.0 mmol; 1-octene, 13.5 mmol; Ru/R_3SiH, 2.5×10^{-4} M; benzene, 5 mL; 65 °C, 3 h, N_2. R_3SiH conversion, 100%. [c] R_3SiH, 3.8 mmol; 1-octene, 4.7 mmol; Pt/R_3SiH, 2.7×10^{-3} M; benzene, 5 mL; 50 °C, 4 h, N_2. R_3SiH conversion, 80%. [d] R_3SiH, 4.7 mmol; 1-octyne, 22.5 mmol; Rh/R_3SiH, 2.3×10^{-3} M; benzene, 5 mL; 60 °C, 2 h, N_2. R_3SiH conversion, 100%. [e] R_3SiH, 2.1 mmol; 1-octyne, 18.2 mmol; Ru/R_3SiH, 2.5 $\times 10^{-4}$ M; toluene, 10 mL; 75 °C, 2 h, N_2. R_3SiH conversion, 100%. [f] R_3SiH, 3.0 mmol; 1-octyne, 18.2 mmol; Pt/R_3SiH, 2.4×10^{-4} M; toluene, 10 mL; 80 °C, 1 h, N_2. R_3SiH conversion, 100%. [g] Selectivity × conversion = yield. [h] Based on silane.

Table II. Diagnostic NMR Data (δ) of Selected Hydrosilylation Products[a]

						
NMR	2a	2b	3a	3b	4	$R_3Si(C_8H_{17})$
^1H	5.62 H_a (d), J_{ab} = 18.3 Hz; 6.06 H_b (d of t), J_{ab} = 18.3; J_{bc} = 6.1 Hz	5.04 H_a (d), J_{ab} = 14.1 Hz; 6.30 H_b (p), J_{ab} = 14.1; J_{bc} = 7.3 Hz	5.20–5.50 H_a, H_b (m)	5.20–5.50 H_a, H_b (m)	5.28 H_a, H_b (d), J_{ab} = 3.2 Hz	
^{13}C	C-1 148.0 (d) C-2 127.7 (d)		C-2 129.3 (d) C-3 126.1 (d)	C-2 128.9 (d) C-3 125.3 (d)		
^{29}Si	−6.07		2.05	2.05		2.70

[a] $R_3 = CH_3(C_{10}H_{21})_2$.

Table III. Hydrosilylation of 1-Decene with Triethylsilane

[Rh(I)], M solvent (mL) temp, °C time, min	8.6×10^{-4} $PhCH_3$ (10)[a] 80–85 60	1×10^{-4} $PhCH_3$ (10)[a] 85–90 30	3.5×10^{-3} $PhCH_3$ (1)[a] 80–84 20	8.8×10^{-4} n-$C_{10}H_{22}$ (10)[a] 84–89 30	8.6×10^{-4} 88–95[b] 15	6.7×10^{-5} 86–90[b] 10	6.7×10^{-6} 105–110[b,c] 19 h	6×10^{-6} 93–100[d] 22 h
products	% molar selectivity, GLC							
5	77	92	69	77	38	53	93[e]	97[f]
6a	12	6	19	10	38	35	3	1
7a	8	2	10	10	20	12	2	1
7b	3	tr	2	3	4	tr	2	1
total unsatd product, %	23	8	31	23	62	47	7	3
Et_3SiH conv, %	70	55	60	74	94	95	71	71

[a] 1-Decene, 20 mmol; Et_3SiH, 9.5 mmol; alkene/silane ratio: 2.1/1. [b] 1-Decene, 63 mmol; Et_3SiH, 9.5 mmol; alkene/silane ratio: 11.5/1. [c] 0.80 mL of 1.2×10^{-3} M $RhCl(PPh_3)_3$ in $PhCH_3$. [d] 1-Decene, 31 mmol; Et_3SiH, 9.5 mmol; alkene/silane ratio: 5.8/1; 1.6 mL of *c* added. [e] Similar result was obtained with [Rh(I)], 1.3×10^{-5} M, 19 h, Et_3SiH conversion, 100%. [f] Similar result was obtained with [Rh(I)], 1.3×10^{-5} M, 1.5 h, Et_3SiH conversion, 96%.

The ratio of **7a**/**7b** formed also remained constant (6.2/1). As the reaction progressed, the ratio of **6a**/(**7a** + **7b**) decreased to 1.1/1 and that of **7a**/**7b** decreased to about 2.7/1, indicating that isomerization was taking place during the later stage of the reaction. It was therefore concluded that part of allylsilanes **7a** and **7b** were formed in competition with vinylsilane **6a** and part were formed via isomerization of **6a**.

Effect of $RhCl(PPh_3)_3$ Concentration. The data in Table III show that Wilkinson's catalyst is an effective hydrosilylation catalyst in concentrations ranging from $\sim 10^{-6}$ to 10^{-3} M, with the lower concentrations requiring higher temperatures and longer reaction times. Considering the first three runs (Table III), carried out at comparable temperature range, the data show that higher catalyst concentrations led to higher proportion of unsaturated product. A similar trend was also evident in the two runs performed by using excess olefin as the solvent.

Experiments with very low rhodium content ($\sim 10^{-6}$ M) proceeded very slowly, even above 100 °C, but gave high selectivities of the saturated product. In this case, not only the low concentration of rhodium but also higher temperatures to be discussed later were expected to favor the monomer form of the catalyst.

Effect of Solvents. The effect of solvents on the composition and structure of chlororuthenium(II) phosphine complexes with trialkylsilanes has been known.[10,11] In our work, the use of toluene or *n*-decane as solvents under similar conditions showed no significant difference in the product distribution. This result would indicate that

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(11) Kono, N.; Wakao, N.; Nagai, Y. *Chem. Lett.* **1975**, 955.
(12) Osborn, J. A.; Jardine, F. H.; Young, J. F.; Wilkinson, G. *J. Chem. Soc. A* **1966**, 1711.

Table IV. Effect of Temperature on Hydrosilylation of 1-Alkenes[a]

alkene	1-hexene	1-heptene	1-octene[b]	1-octene[b]
[Rh(I)], M	1.2×10^{-3}	1.1×10^{-3}	9.7×10^{-4}	9.7×10^{-4}
temp,[d] °C	64–65	94–95	61–62	99–100
time,[c] min	40	15	75	35
products	% molar selectivity, GLC			
5	31	75[e]	60	79[e]
6a	55	19	28	14
7a + 7b	14	6	12	7
total unsatd product, %	69	25	40	21
Et_3SiH conv, %	99	97	75	91

[a] 1-Alkene/Et_3SiH ratio, 6.5/1, mol/mol. [b] Under sufficient vacuum to cause alkene to reflux. [c] Arbitrary value. [d] Reflux temperatures. [e] Typical values.

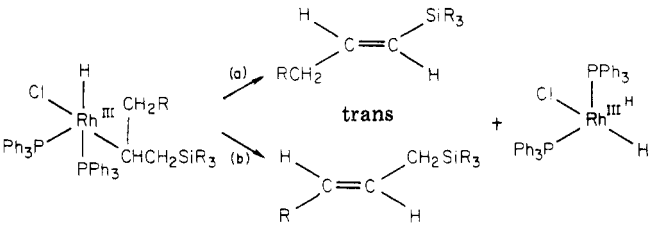
solvents are not that critical in the rhodium system or that both solvents were behaving in a similar manner, in spite of their different physical properties. On the other hand, experiments carried out with excess alkene as the solvent gave much higher proportion of unsaturated products than had been anticipated. This may be interpreted to be the result of coordination of olefin to the rhodium metal, prior to oxidative addition of the silane to the metal.

Effect of Temperature. To determine the effect of temperature on the course of hydrosilylation reaction (Table IV), experiments were carried out under conditions where the alkene would reflux. In this manner, only small variations in temperature were observed, in spite of highly exothermic nature of the reaction, particularly in the presence of high catalyst concentrations. The results show that higher temperatures favor the formation of saturated product, which is in contrast to that observed with osmium catalyst.[1] The values for the unsaturated product obtained at higher temperatures probably are the maximum values. This is because the reaction with a high concentration of rhodium already starts to occur at a low temperature, and the distribution of products obtained at higher temperature depends on the rate of heat up; i.e., if the reaction mixture was heated slowly, most of the reaction may be over by the time the desired high temperature is reached, and the distribution of product obtained may be a reflection of the effect of lower temperature. The preferred formation of the saturated product at higher temperature is consistent with the importance of rhodium monomer–dimer equilibrium, the higher temperature favoring the monomer form of the catalyst.

Relative Reactivity. Measurements of competitive reaction rate at both the low and high catalyst loadings (8.5×10^{-5} and 3.5×10^{-3} M, respectively) showed that 1-decene was of about the same order of reactivity toward triethylsilane as styrene (1 ± 0.2), while α-methylstyrene, β-methylstyrene, and 2-ethyl-1-hexene were essentially unreactive. This order of reactivity is not the one expected for a typical free radical or ionic addition, but is consistent with a cis covalent type addition.[13] The low reactivity of substituted styrenes and of vinylidene olefin in the rhodium system was attributed to steric factors that apparently prevent contact between the double bond and the catalyst. In the reaction of triethylsilane with styrene, 1-(triethylsilyl)- and 2-(triethylsilyl)-1-phenylethanes were formed about 2–3 times as fast as *trans*-$Et_3SiCH{=}CHPh$, in spite of the 40-fold excess of catalyst in the latter.[5] This result is consistent with the importance of rhodium monomer-dimer equilibrium, the lower concentration favoring

(13) Heck, R. F. *J. Am. Chem. Soc.* **1969**, *91*, 6707.

Scheme I



cis and trans

the monomer form of rhodium. This phenomenon has been adequately discussed by Wilkinson et al.[12] If the equilibrium postulate is accepted, it is apparent that monomeric rhodium gives the saturated hydrosilylation product at a fast rate, while the dimeric rhodium gives the unsaturated products at a slower rate.

Mechanism. While detailed elucidation of the reaction mechanism is beyond the scope of present investigation, the data obtained thus far are consistent with the importance of rhodium monomer–dimer equilibrium, as suggested earlier for styrene.[5] In the present work, the key intermediate is believed to be the Rh(III) complex that undergoes β-hydride elimination in two directions to give the unsaturated products (Scheme I).[14]

Note Added in Proof. A dramatic example of the importance of monomeric–dimeric species as a function of catalyst concentration has recently appeared (Patil, S. R.; Chaudhari, R. V.; Sen, D. N. *J. Mol. Catal.* **1984**, *23*, 51). Use of homogeneous catalyst solutions of $RuCl_2(PPh_3)_3$ in the hydrogenation of cyclohexene revealed a catalyst concentration dependence of reaction rate at ca. 8.4×10^{-4} M attributed to formation of dimeric species, strikingly similar to our findings. These results strongly support our mechanistic inferences.

Experimental Section

Hydrosilylation reactions were carried out at atmospheric pressure in a standard laboratory glassware under nitrogen. Chromatographic analyses were performed on a Hewlett-Packard 5880A (FID) chromatograph, employing a 10-m or 25-m, 2% OV-101, fused silica capillary column, programmed from 50 to 300 °C at 8°/min, and a 50-m, Carbowax 20M fused silica capillary column, programmed from 70 to 220 °C at 4°/min. The ^1H NMR spectra were obtained on a Varian T-60 or XL-200 spectrometer, usually in carbon tetrachloride or acetone-d_6. The chemical shifts are in δ units (ppm), relative to Me_4Si (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet). The IR spectra were recorded on a Perkin-Elmer Model 597 spectrometer. GC/MS data were obtained on a Finnigan 4510 system with an electron-impact source at 70 eV. $RhCl(PPh_3)_3$ was obtained from Engelhard Industries. The following procedure is representative of the reaction of alkenes (and alkynes) with silanes (see footnotes of Tables I, III, and IV for conditions).

Reaction of Methyldi-*n*-decylsilane with 1-Octene. A 100-mL, three-necked, round-bottomed flask, fitted with a condenser connected to a nitrogen source, a thermometer, and a serum cap, was charged with 1-octene (22.3 mmol), methyldi-*n*-decylsilane (4.7 mmol), chlorotris(triphenylphosphine)rhodium(I) (10 mg, $1.0, \times 10^{-2}$ mmol), and benzene (5 mL). After the system was purged with nitrogen for 15 min, the mixture was heated to 70 °C and was allowed to proceed for 2 h, monitoring the course of reaction by periodic withdrawal of samples for GLC analysis.

(14) One of the reviewers suggested that an alternate mechanism to the monomer–dimer equilibrium involves substitution of x triphenylphosphine ligands by x olefin molecules to generate an intermediate species such as $(Ph_3P)_{3-x}(olefin)_xRhSiH$. High ratios of olefin/Rh would favor higher values of x in the catalytic complex. Higher temperatures favor higher values for x. Rates and ratios of products are a function of x and temperature. We thank the reviewer for this suggestion, which we view as an acceptable alternative to our proposed mechanism.

When the reaction was terminated, the solution was cooled and then passed over short alumina columm (80–100 mesh) to remove most of the catalyst. The unreacted alkenes and the solvent were distilled off under vacuum into a cold trap and analyzed by GLC: *n*-octane, 14.2%; 1-octene, 64.0%; *trans*-2-octene, 15.7%; *cis*-2-octene, 6.1%. The yield of *n*-octane, based on silane, corresponded to 38%. The product (1.95 g, 95%) was analyzed by GLC, IR, and NMR (Table II). Hydrogenation of the product ($RhCl(PPh_3)_3$, $PhCH_3$, 70 °C, 2–3 atm of H_2, 3.5 h) gave tetraalkylsilane: ^{29}Si NMR δ 2.70; mass spectrum, *m/e* (% relative intensity) 438 (0, P^+), 423 (0.1, P - $CH_3)^+$, 325 (26, $CH_3Si^+(C_{10}H_{21})_2$), 297 (64, $CH_3Si^+(C_8H_{17})(C_{10}H_{21})$), 185 (100, $CH_3Si^+(H)(C_{10}H_{21})$), 157 (60, $CH_3Si^+(H)(C_8H_{17})$), 113 (41, $CH_3Si^+(H)C_5H_9$)), 99 (33, $CH_3Si^+(H)C_4H_7$)), 85 (28, $CH_3Si^+(H)C_3H_5$)), 73 (29, $CH_3Si^+(H)C_2H_5$)), 59 (18, $CH_3Si^+(H)CH_3$)), 45 (5, $CH_3Si^+H_2$). Anal. Calcd for $C_{29}H_{62}Si$: C, 79.36; H, 14.24. Found: C, 79.41; H, 14.26.

Preparation of Methyldi-*n*-decylsilane. Into a 2-L, four-necked flask, equipped with a mechanical stirrer, reflux condensor, addition funnel, and a thermometer, was added magnesium chips (28.4 g, 1.17 mol) and several crystals of iodine. The flask, while vigorously stirred, was heated to about 50° C under nitrogen for 30 min and cooled. After addition of 100 mL of diethyl ether and 20 mL of 1-bromodecane solution (198.5 g of 1-bromodecane in 720 mL of THF), the reaction began almost immediately as noted by a temperature rise of 5 °C. The addition of halide was continued over 4 h, while a temperature of 25–30 °C was maintained, and the mixture was stirred overnight. Titration of an aliquot with hydrochloric acid showed that 0.88 mol of Grignard reagent was formed. After filtration (N_2 blanket) and washing of magnesium turnings with THF, methyldichlorosilane (51.0 g, 0.44 mol) dissolved in THF (170 mL) was added to the filtrate over 2 h, maintaining a temperature of 35–40 °C. The reaction mixture was then heated at 62 °C for 12 h, cooled, poured over cracked ice, and hydrolyzed with 1 N HCl. After extraction with ether, washing with water, drying ($MgSO_4$), and evaporation of ether gave 133.2 g of product. Analysis by GLC indicated the presence of *n*-eicosane (6.3%), 1-decanol (17.9%), and methyldi-*n*-decylsilane (75.0%) as major products. Distillation gave one major fraction, bp 200 °C (0.3 mmHg), which corresponded to a 23% yield of methyldi-*n*-decylsilane: IR 2100 cm^{-1}s, SiH; NMR δ 3.7 (m, 1 H, SiH), 1.3 (s, 32 H, CH_2), 0.9 (distorted t, 6 H, CH_3CH_2), 0.57 (m, 4 H, $SiCH_2$), 0.05 (s, 3 H, $SiCH_3$); GLC 99% purity; ^{29}Si NMR δ -9.85.

Mass Spectra of Products from the Reaction of Triethylsilane with 1-Hexene (Table IV, first entry): $Et_3SiC_6H_{13}$, *m/e* (relative intensity) 200 (0, M^+), 171 (77, (M - Et)$^+$), 143 (27), 115 (27), 101 (15), 87 (100), 59 (27); *trans*-$Et_3SiCH{=}CHC_4H_9$, *m/e* (relative intensity) 198 (5, M^+), 169 (100, (M - Et)$^+$), 141 (95), 113 (28), 85 (15), 59 (15); the corresponding cis isomer had the same major ions; *trans*-$Et_3SiCH_2CH{=}CHC_3H_7$, 198 (11, M^+), 169 (3, (M - Et)$^+$), 115 (100, Et_3Si^+), 87 (97), 59 (25); the corresponding cis isomer had the same major ions.

Effect of Solvents. In present work, *n*-decane, toluene, and excess olefin were used as solvents. These experiments were carried out by employing the basic procedure previously described for the hydrosilylation of methyldi-*n*-decylsilane with 1-octene. The reaction conditions, reactant ratios, and other information are given in Table III as footnotes.

Relative Reactivity. Relative reactivity of olefins with methyldi-*n*-decylsilane was carried out in a competitive experiment using equimolar ratio of 1-decene and styrene in benzene solvent, which also served as internal standard. The reactivities were based on the disappearance of the starting olefins.

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Registry No. 1, 83584-71-8; **2a**, 90584-14-8; **2b**, 90584-15-9; **3a**, 90584-16-0; **3b**, 90584-17-1; **4**, 90584-18-2; **5**, 18408-00-9; **6a**, 90584-19-3; **7a**, 90605-21-3; **7b**, 90605-22-4; $RhCl(PPh_3)_3$, 14694-95-2; $Ru_3(CO)_{12}$, 15243-33-1; H_2PtCl_6, 16941-12-1; $Et_3SiC_6H_{13}$, 13810-04-3; *trans*-$Et_3SiCH{=}CHC_4H_9$, 42067-72-1; *cis*-$Et_3SiCH{=}CHC_4H_9$, 62621-38-9; *trans*-$Et_3SiCH_2CH{=}CHC_3H_7$, 79643-98-4; *cis*-$Et_3SiCH_2CH{=}CHC_3H_7$, 90584-20-6; methyldi(*n*-decyl)silane, 51502-65-9; triethylheptylsilane, 18414-81-8; *trans*-triethyl-1-heptenylsilane, 53335-87-8; *trans*-triethyl-2-heptenylsilane, 90584-21-7; *cis*-triethyl-2-heptenylsilane, 90584-22-8; triethylsilane, 617-86-7; methyldichlorosilane, 75-54-7; 1-octene, 111-66-0; 1-octyne, 629-05-0; 1-decene, 872-05-9; *n*-octane, 111-65-9; *trans*-2-octene, 13389-42-9; *cis*-2-octene, 7642-04-8; 1-bromodecane, 112-29-8; *n*-eicosane, 112-95-8; 1-decanol, 112-30-1; 1-hexene, 592-41-6; 1-heptene, 592-76-7.

Synthesis of 1-Acyl-1,4-dihydropyridines via Copper Hydride Reduction of 1-Acylpyridinium Salts

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For many years there has been considerable interest in the synthesis, synthetic utility, and biological activity of various dihydropyridines.[1] The discovery that a 1-acyl substituent stabilizes[2,3] the dihydropyridine system has encouraged the study and use of 1-acyldihydropyridines as synthetic intermediates. Although 1-(alkoxycarbonyl)-1,2-dihydropyridines can be prepared by a regioselective sodium borohydride reduction of 1-(alkoxycarbonyl)pyridinium salts,[3] a regioselective reduction to give 1-acyl-1,4-dihydropyridines has not been reported.

Alkyl Grignard reagents add to 1-acylpyridinium salts to give a mixture of 1,2- and 1,4-dihydropyridines;[4a,5] however, when a catalytic amount of cuprous iodide is present, the addition is regiospecific and nearly exclusive 1,4-addition results.[4] Stoichiometric organocopper reagents (e.g., R_2CuLi, RCu, $RCu{\cdot}BF_3$) also give 1,4-addition.[6] On the basis of these results, it appeared that an analogous 1,4-addition of hydride to 1-acylpyridinium salts might occur with copper hydride reagents and effect a regiospecific one-pot synthesis of 1-acyl-1,4-dihydropyridines.

We report herein our study on the reduction of 1-(phenoxycarbonyl)pyridinium chloride with copper(I) borohydride and copper hydride reagents, which led to the development of a convenient method for the regiospecific synthesis of 1-acyl-1,4-dihydropyridines. The regioselectivity of the reduction of 1-(phenoxycarbonyl)pyridinium chloride[7] with various hydride reagents is shown in Table

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