The Direct Conversion of α-Olefins into Vinyl- and Allyl-silanes catalysed by Rhodium Complexes

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Summary At high α-olefin to Et_3SiH ratios and at temperatures ⩽40 °C $[(RhC_5Me_5)_2Cl_4]$ catalyses the formation of vinyl- and allyl-silanes; other rhodium complexes act similarly.

WHILE the transition metal complex-catalysed hydrosilylation of terminal olefins is a well established reaction (A)[1] only scattered reports have appeared concerning the coproduction of vinylsilanes.[2–5] Most of those have related to the formation of styrylsilanes from the reactions of styrene (or substituted styrenes) with R_3SiH.[2–4] The current interest in vinylsilanes as organic synthons[6] prompts us to report our results on an efficient direct conversion of α-olefins into unsaturated silanes and on the conditions needed to accomplish this.

$$\mathrm{RCH{=}CH_2 + R'_3SiH \rightarrow RCH_2CH_2SiR'_3} \qquad \text{(A)}$$

For most of these experiments we have used $[(RhC_5Me_5)_2Cl_4]$[7,8] as the catalyst but we have also found that very similar results are given by the Wilkinson complex $[Rh(PPh_3)_3Cl]$ under similar conditions.

Using hex-l-ene as a model α-olefin, and Et_3SiH as the silicon hydride we were able to characterise three products, n-hexyl(triethyl)silane (**1**), (*E*)-hex-l-enyl(triethyl)silane (**2**), and (*E*)-hex-2-enyl(triethyl)silane (**3**);† n-hexane was also formed and evidence for the isomerisation of hex-l-ene to internal olefins was found.

$$\mathrm{CH_3[CH_2]_4CH{=}CH_2 + Et_3SiH \rightarrow}$$
$$\underset{(\mathbf{1})}{\mathrm{CH_3{}^{a}CH_2{}^{b}CH_2{}^{c}CH_2{}^{d}CH_2{}^{e}CH_2{}^{f}Si(CH_2{}^{g}CH_3{}^{h})_3}} +$$
$$\underset{(\mathbf{2})}{\mathrm{CH_3{}^{a}CH_2{}^{b}CH_2{}^{c}CH_2{}^{d}CH^{e}{=}CH^{f}Si(CH_2{}^{g}CH_3{}^{h})_3}} +$$
$$\underset{(\mathbf{3})}{\mathrm{CH_3{}^{a}CH_2{}^{b}CH_2{}^{c}CH^{d}{=}CH^{e}CH_2{}^{f}Si(CH_2{}^{g}CH_3{}^{h})_3}}$$
$$+ \mathrm{CH_3[CH_2]_4CH_3}$$

The relative ratios (**1**) : (**2**) : (**3**) were investigated as a function of several variables. Those which had the greatest effect were (a) the initial ratio of hexene : Et_3SiH and (b) the reaction temperature. Oxygen, traces of water, and different levels of catalyst had only very minor effects for $[(RhC_5Me_5)_2Cl_4]$.

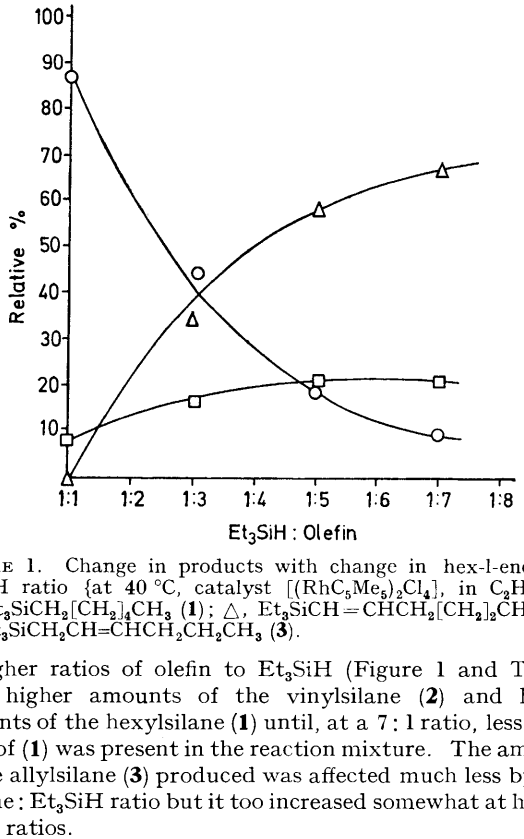

FIGURE 1. Change in products with change in hex-l-ene and Et_3SiH ratio {at 40 °C, catalyst $[(RhC_5Me_5)_2Cl_4]$, in $C_2H_4Cl_2$}. ○, $Et_3SiCH_2[CH_2]_4CH_3$ (**1**); △, $Et_3SiCH{=}CHCH_2[CH_2]_2CH_3$ (**2**); □, $Et_3SiCH_2CH{=}CHCH_2CH_2CH_3$ (**3**).

Higher ratios of olefin to Et_3SiH (Figure 1 and Table) gave higher amounts of the vinylsilane (**2**) and lower amounts of the hexylsilane (**1**) until, at a 7 : 1 ratio, less than 10% of (**1**) was present in the reaction mixture. The amount of the allylsilane (**3**) produced was affected much less by the hexene : Et_3SiH ratio but it too increased somewhat at higher olefin ratios.

On increasing the reaction temperature from 40 to 100 °C the amount of vinylsilane (**2**) decreased sharply with simultaneous increases in the amounts of (**1**) and (**3**) (Figure 2).

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† ^1H N.m.r. spectra (400 MHz) in $CDCl_3$: (**1**) δ 0·50 [q, $CH_2{}^{g}$, $J(H^{g}H^{h})$ 8 Hz], 0·92 (t, $CH_3{}^{h}$, $CH_3{}^{a}$), and 1·28 (broad s, $CH_2{}^{b,c,d,e}$); (**2**) δ 0·50 (q, $CH_2{}^{g}$), 0·92 (t, $CH_3{}^{h}$), 1·28 (broad s, $CH_2{}^{b,c}$), 2·11 (dt, $CH_2{}^{d}$), 5·52 (d, CH^{f}), and 6·03 (dt, CH^{e}); $J(H^{e}H^{f}) = 19$, $J(H^{c}H^{d}) = J(H^{d}H^{e}) = 7$, $J(H^{g}H^{h}) = 8$, $J(H^{d}H^{f}) = 1$ Hz; (**3**) δ 0·50 (q, $CH_2{}^{g}$), 0·88 (t, $CH_3{}^{a}$), 0·92 (t, $CH_3{}^{h}$), 1·35 (tq, $CH_2{}^{b}$), 1·43 (d, $CH_2{}^{f}$), 1·95 (dt, $CH_2{}^{c}$), 5·25 (dt, CH^{d}), and 5·37 (dt, CH^{e}); $J(H^{a}H^{b}) = J(H^{b}H^{c}) = J(H^{c}H^{d}) = J(H^{e}H^{f}) = 7$, $J(H^{g}H^{h}) = 8$, $J(H^{d}H^{e}) = 15$ Hz.

TABLE

Reactant $RCH_2CH{=}CH_2$	Catalyst[b]	Time /h	Ratio olefin: Et_3SiH	Total yield (%)	Products (%)[a] $RCH_2CH_2CH_2SiEt_3$	$RCH_2CH:CHSiEt_3$	$RCH:CHCH_2SiEt_3$
R = Pr^n	A	1	1:1	40	87	0	8
	A	1	3:1	90	44	35	16
	A	1	5:1	95	19	58	21
	A	1	7:1	95	10	67	21
	B	1	5:1	90	25	50	22
	C	6	5:1	93	53	31	15
	D	0·67	11:1	75	100	0	0
R = Bu^n	A	4	5:1	90	34	52	8
R = n-C_6H_{13}	A	6	3:1	98	34	46	20
$PhCH{=}CH_2$	A	72	5:1	90	$PhCH_2CH_2SiEt_3$ 25% $PhCH{=}CHSiEt_3$ 55% unidentified 20%		

[a] Characterised and analysed by ^1H n.m.r. spectroscopy (220 MHz), g.l.c., and mass spectrometry. [b] A = $[(RhC_5Me_5)_2Cl_4]$ (0·01 mmol), Et_3SiH (7·5 mmol), solvent $C_2H_4Cl_2$ (9 cm^3), at 40 °C. B = $[Rh(PPh_3)_3Cl]$ (0·005 mmol), Et_3SiH (7·5 mmol), solvent $C_2H_4Cl_2$, (9 cm^3), at 40 °C. C = $[Rh(acac)_3]$ (0·1 mmol), Et_3SiH (15 mmol), solvent $C_2H_4Cl_2$, (9 cm^3), at 40 °C. D = $[Pt_2(C_2H_4)_2Cl_4]$ (0·01 mmol), Et_3SiH (7·5 mmol), solvent $C_2H_4Cl_2$ (9 cm^3), at 40 °C.

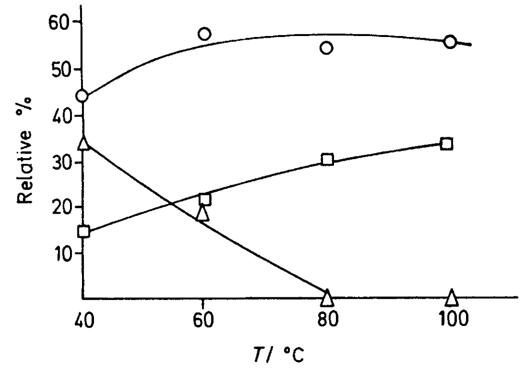


FIGURE 2. Change in products with temperature for reaction of hex-l-ene and Et_3SiH {ratio 3:1, catalyst $[(RhC_5Me_5)_2Cl_4]$ in $C_2H_4Cl_2$}. ○, $Et_3SiCH_2[CH_2]_4CH_3$ (**1**); △, $Et_3SiCH{=}CHCH_2[CH_2]_2CH_3$ (**2**); □, $Et_3SiCH_2CH{=}CHCH_2CH_2CH_3$ (**3**).

The solvent normally used was 1,2-dichloroethane; the reactions could also be carried out in benzene and entirely without solvent with similar results, but problems due to catalyst insolubility did complicate these reactions. By contrast, $[Rh(acac)_3]$ (Hacac = pentane-2,4-dione) was found to be a poorer catalyst and also gave lower yields of (**2**) and (**3**). The Speier-type catalyst, $[Pt_2(C_2H_4)_2Cl_4]$,[1,9] while giving a very good rate of reaction, produced only (**1**) and none of the unsaturated silanes (**2**) or (**3**).

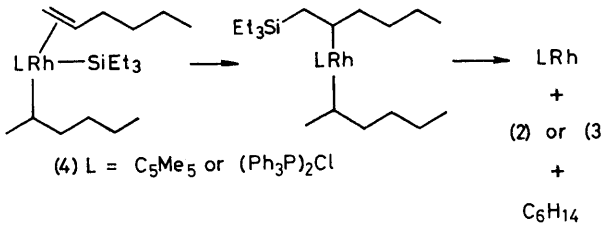
Several other α-olefins were examined and found to react similarly to hex-l-ene (Table). In addition propene, when bubbled (1 atm) through a solution of $[(RhC_5Me_5)_2Cl_4]$ in dichloroethane at 22 °C, very readily gave a 1:1 mixture of $CH_3CH_2CH_2SiEt_3$ and $CH_3CH{=}CHSiEt_3$ (analysed by g.l.c. and ^1H n.m.r. spectroscopy). In the reactions involving non-l-ene, several unsaturated materials in addition to the allyl- and vinyl-silanes were observed.

Proposals for a mechanism will be presented in the full paper but we note that the formation of hexane in an amount corresponding approximately to the total of hexenylsilanes produced suggests that a hydrogen-transfer reaction (C) is taking place, in competition with the normal hydrosilation (B).

$$\text{hex-l-ene} + Et_3SiH \xrightarrow{\text{catalyst}} \text{n-}C_6H_{13}SiEt_3 \qquad \text{(B)}$$

$$2\ \text{hex-l-ene} + Et_3SiH \xrightarrow{\text{catalyst}} \text{n-}C_6H_{11}SiEt_3 + \text{n-}C_6H_{14} \qquad \text{(C)}$$

The increase in unsaturated silanes at high olefin ratios further suggests that the formation of the unsaturated products proceeds *via* intermediates of the type (**4**) containing an olefin co-ordinated to an alkyl–silyl–rhodium centre.



SCHEME

A possible route for breakdown of (4) is given in the Scheme.

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