J.C.S. Снем. Сомм., 1981

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

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Summary At high  $\alpha$ -olefin to Et<sub>3</sub>SiH ratios and at temperatures  $\leq 40$  °C [(RhC<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Cl<sub>4</sub>] 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)<sup>1</sup> only scattered reports have appeared concerning the coproduction of vinylsilanes.<sup>2-5</sup> Most of those have related to the formation of styrylsilanes from the reactions of styrene (or substituted styrenes) with R<sub>3</sub>SiH.<sup>2-4</sup> The current interest in vinylsilanes as organic synthons<sup>6</sup> prompts us to report our results on an efficient direct conversion of  $\alpha$ -olefins into unsaturated silanes and on the conditions needed to accomplish this.

$$RCH = CH_2 + R'_{3}SiH \rightarrow RCH_2CH_2SiR'_{3}$$
(A)

For most of these experiments we have used  $[(RhC_5Me_5)_2-Cl_4]^{7,8}$  as the catalyst but we have also found that very similar results are given by the Wilkinson complex  $[Rh(PPh_a)_3Cl]$  under similar conditions.

Using hex-l-ene as a model  $\alpha$ -olefin, and Et<sub>3</sub>SiH 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.

$$\begin{array}{rl} {\rm CH}_3[{\rm CH}_2]_4{\rm CH}\!=\!{\rm CH}_2 &+& {\rm Et}_3{\rm SiH} \rightarrow \\ {\rm CH}_3{}^{\rm a}{\rm CH}_2{}^{\rm b}{\rm CH}_2{}^{\rm c}{\rm CH}_2{}^{\rm d}{\rm CH}_2{}^{\rm e}{\rm CH}_2{}^{\rm f}{\rm Si}({\rm CH}_2{}^{\rm g}{\rm CH}_3{}^{\rm h})_3 &+\\ & (1) \\ {\rm CH}_3{}^{\rm a}{\rm CH}_2{}^{\rm b}{\rm CH}_2{}^{\rm c}{\rm CH}_2{}^{\rm d}{\rm CH}^{\rm e}\!=\!{\rm CH}{}^{\rm f}{\rm Si}({\rm CH}_2{}^{\rm g}{\rm CH}_3{}^{\rm h})_3 &+\\ & (2) \\ {\rm CH}_3{}^{\rm a}{\rm CH}_2{}^{\rm b}{\rm CH}_2{}^{\rm c}{\rm CH}{}^{\rm d}\!=\!{\rm CH}{}^{\rm e}{\rm CH}_2{}^{\rm f}{\rm Si}({\rm CH}_2{}^{\rm g}{\rm CH}_3{}^{\rm h})_3 &+\\ & (3) \\ &+& {\rm CH}_3[{\rm CH}_2]_4{\rm CH}_3 \end{array}$$

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<sub>5</sub>-Me<sub>5</sub>)<sub>2</sub>Cl<sub>4</sub>].



FIGURE 1. Change in products with change in hex-l-ene and Et\_3SiH ratio {at 40 °C, catalyst [(RhC<sub>5</sub>Me\_5)\_2Cl\_4], in C\_2H\_4Cl\_2 }.  $\bigcirc$ , Et\_3SiCH\_2[CH\_2]\_4CH\_3 (1);  $\bigcirc$ , Et\_3SiCH=CHCH\_2[CH\_2]\_2CH\_3 (2);  $\square$ , Et\_3SiCH\_2CH=CHCH\_2CH\_2CH\_3 (3).

Higher ratios of olefin to  $\text{Et}_3\text{SiH}$  (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:  $\text{Et}_3\text{SiH}$  ratio but it too increased somewhat at higher olefin ratios.

On increasing the reaction temperature from 40 to  $100 \,^{\circ}$ C the amount of vinylsilane (2) decreased sharply with simultaneous increases in the amounts of (1) and (3) (Figure 2).

<sup>&</sup>lt;sup>†</sup><sup>1</sup>H N.m.r. spectra (400 MHz) in CDCl<sub>3</sub>: (1)  $\delta 0.50$  [q, CH<sub>2</sub><sup>g</sup>,  $J(H^gH^h) 8 Hz$ ], 0.92 (t, CH<sub>3</sub><sup>h</sup>, CH<sub>3</sub><sup>a</sup>), and 1.28 (broad s, CH<sub>2</sub><sup>b,c,d,e</sup>); (2)  $\delta 0.50$  (q, CH<sub>2</sub><sup>g</sup>), 0.92 (t, CH<sub>3</sub><sup>h</sup>), 1.28 (broad s, CH<sub>2</sub><sup>b,c)</sup>, 2.11 (dt, CH<sub>2</sub><sup>d</sup>), 5.52 (d, CH<sup>t</sup>), and 6.03 (dt, CH<sup>e</sup>);  $J(H^eH^t) = 19$ ,  $J(H^eH^d) = J(H^aH^e) = 7$ ,  $J(H^gH^h) = 8$ ,  $J(H^dH^f) = 1 Hz$ ; (3)  $\delta 0.50$  (q, CH<sub>2</sub><sup>g</sup>), 0.88 (t, CH<sub>3</sub><sup>a</sup>), 0.92 (t, CH<sub>3</sub><sup>h</sup>), 1.35 (tq, CH<sub>2</sub><sup>b</sup>), 1.43 (d, CH<sub>2</sub><sup>t</sup>), 1.95 (dt, CH<sub>2</sub><sup>c</sup>), 5.25 (dt, CH<sup>d</sup>), and 5.37 (dt, CH<sup>e</sup>);  $J(H^aH^b) = J(H^eH^d) = J(H^eH^t) = 7$ ,  $J(H^gH^h) = 8$ ,  $J(H^dH^e) = 15$  Hz.

				1 ABLE			
Decetort		Time /h	Ratio olefin : Et <sub>3</sub> SiH	Total yield (%)	Products (%)a		
$RCH_2CH = CH_2$	Catalystb				RCH2CH2CH2SiEt3	RCH <sub>2</sub> CH : CHSiEt <sub>3</sub>	RCH: CHCH_SiEt
$R = Pr^n$	A A A B C D	1 1 1 1 6 0.67	1:1 3:1 5:1 7:1 5:1 5:1	40 90 95 95 90 93 75	87 44 19 10 25 53 100	0 35 58 67 50 31 0	8 16 21 21 22 15 0
$\begin{array}{l} R = Bu^n \\ R = n \cdot C_8 H_{13} \\ PhCH=CH_2 \end{array}$	A A A	4 6 72	5:1 3:1 5:1	90 98 90	34 34 PhCH <sub>2</sub> CH <sub>2</sub> SiEt <sub>3</sub> 25 % PhCH=CHSiEt <sub>3</sub> 55 % unidentified 20 %	52 46	8 20

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<sup>a</sup> Characterised and analysed by <sup>1</sup>H n.m.r. spectroscopy (220 MHz), g.l.c., and mass spectrometry. <sup>b</sup> A = [(RhC<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Cl<sub>4</sub>] (0·01 mmol), Et<sub>3</sub>SiH (7·5 mmol), solvent C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> (9 cm<sup>3</sup>), at 40 °C. B = [Rh(PPh<sub>3</sub>)<sub>3</sub>Cl] (0·005 mmol), Et<sub>3</sub>SiH (7·5 mmol), solvent C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>, (9 cm<sup>3</sup>), at 40 °C. C = [Rh(acac)<sub>3</sub>] (0·1 mmol), Et<sub>3</sub>SiH (15 mmol), solvent C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>, (9 cm<sup>3</sup>), at 40 °C. D = [Pt<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>Cl<sub>4</sub>] (0·01 mmol), Et<sub>3</sub>SiH (7·5 mmol), solvent C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> (9 cm<sup>3</sup>), at 40 °C.



FIGURE 2. Change in products with temperature for reaction of hex-lene and Et\_siH fratio 3:1, catalyst [[RhC<sub>9</sub>Me<sub>9</sub>]<sub>2</sub>Cl<sub>4</sub>] in C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>}.  $\bigcirc$ , Et\_3SiCH<sub>2</sub>[CH<sub>2</sub>]<sub>4</sub>CH<sub>3</sub> (1);  $\triangle$ , Et<sub>3</sub>SiCH<sub>2</sub>=CHCH<sub>2</sub>-[CH<sub>2</sub>]<sub>4</sub>CH<sub>3</sub> (2);  $\Box$ , Et<sub>3</sub>SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> (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,  $[Pt_2(C_2H_4)_2Cl_4]$ ,<sup>1,9</sup> while giving a very good rate of reaction, produced only (1) and none of the unsaturated silanes (2) or (3).

Several other  $\alpha$ -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<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Cl<sub>4</sub>] 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 <sup>1</sup>H 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).

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

catalyst  $\longrightarrow$  n-C<sub>6</sub>H<sub>11</sub>SiEt<sub>3</sub> + n-C<sub>6</sub>H<sub>14</sub> (C)  $2 \text{ hex-l-ene} + \text{Et}_3 \text{SiH} -$ 

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.

We thank Conicit (Venezuela) for a studentship (for A.M.) and the S.R.C. for support.

(Received, 1st April 1981; Com. 375.)

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