HYDROSILYLATION OF 1-PENTYNE BY TRIETHYLSILANE CATALYZED BY PHOSPHINE-RHODIUM COMPLEXES

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Summary:
The hydrosilylation of 1-pentyne by triethylsilane has been investigated using rhodium catalysts, formed by displacement of cyclooctene from dichlorotetrakis(cyclooctene)dirhodium(I) by various molar ratios of phosphines. The results are interpreted in terms of isomerization of an intermediate vinylrhodium complex.

Article:
Introduction
The hydrosilylation of 1-hexyne by triethylsilane catalyzed by chloroplatinic acid or octacarbonyldicobalt(0) has been reported to yield *trans*-1-triethylsilyl-1-hexene and 2-triethylsilyl-1-hexene (eq. 1) [1,2]. The *trans*-1-triethylsilyl-1- hexene being formed by *cis*-addition of the silane. However, recent results have trans-olefin being sensitive to factors such as catalyst concentration and temperature [3,4]. Originally it was suggested that the *cis*-olefin was formed by *trans*-addition [3]. However, later results suggested that only *cis*-addition to yield the trans-olefin was occurring, followed by rhodium-catalyzed *trans*-*cis* isomerization to account for the formation of *cis*-olefin [4]. This seems plausible, as it is difficult to write a mechanism for *trans*-addition and rhodium complexes are known to be good isomerization catalysts. However, in the hydrosilylation of phenylacetylene by dimethylphenylsilane catalyzed by $[RhCl(PPh_3)_3]$ it was reported that extensive isomerization of the *cis*-olefin to the *trans*-olefin occurred [5].

$$\text{n-BuC}\equiv\text{CH} + \text{HSiEt}_3 \rightarrow \textit{trans}\text{-n-BuCH}=\text{CHSiEt}_3 + \text{Bu}^{\text{n}}(\text{Et}_3\text{Si})\text{C}=\text{CH}_2 \qquad (1)$$

shown that chlorotris(triphenylphosphine)rhodium(I) yields a mixture of *cis*- and *trans*-1-triethylsilyl-1-hexenes (eq. 2), with the relative amounts of *cis*- and

$$\text{n-BuC}\equiv\text{CH} + \text{HSiEt}_3 \rightarrow \textit{cis}\text{- and }\textit{trans}\text{-n-BuCH}=\text{CHSiEt}_3 \qquad (2)$$

We report here on our studies of the hydrosilylation of 1-pentyne by triethylsilane catalyzed by phosphine-rhodium(I) complexes formed in situ from dichlorotetrakis(cyclooctene)rhodium(I) and varying molar ratios of phosphines.

Results and discussion
1-Pentyne was hydrosilylated by triethylsilane catalyzed by a variety of phosphine-rhodium(I) complexes, leading to *trans*- and *cis*-1-triethylsilyl-1-pentenes, I and II, which were isolated by preparative GLC, and a third isomer, III in small amounts (5-10%) which could not be isolated by preparative GLC. Similar difficulties in isolating the third isomer have been reported by other workers [4]. The third isomer was not the internal adduct, 2-triethylsilyl-1- pentene, as it had a different GLC retention time. It did, however, have the same GLC retention time as 1-triethylsilyl-2-pentene. This could, perhaps, form by isomerization of the initially formed terminal adducts.

We were interested in investigating the variations in proportions of the two isomers, as the nature of the catalyst was changed. The catalyst system was produced by adding appropriate quantities of ligands, L, to $[RhCl(C_8H_{14})_2]_2$ thus generating the species L_nRhCl in situ.

Using triphenylphosphine as a ligand, the ratio of PPh_3/Rh was varied from 0 to 4, for the hydrosilylation of 1-pentyne by triethylsilane. The results are summarized in Table 1. As can be seen from Table 1, the yield of pentenylsilanes reaches a maximum at a ratio of PPh_3/Rh of 0.5/1, and falls off rapidly as the amount of phosphine is increased. It is surprising that at a PPh_3/Rh ratio of 3/1, which would be expected to generate Wilkinson's catalyst in situ, the yield is lower than with no PPh_3 at all. This suggests that equilibria of the type illustrated in eq. 4 or 5 are of great importance and that added triphenylphosphine,

$$(PPh_3)_nRhCl + HSiEt_3 \rightleftharpoons HRh(SiEt_3)(PPh_3)_{n-1} + PPh_3 \quad (4)$$

$$(PPh_3)_nRhCl + RC{\equiv}CH \rightleftharpoons (RC{\equiv}CH)Rh(PPh_3)_{n-1} + PPh_3 \quad (5)$$

even at very low ratios (greater than 1.0/1), causes the reaction to become less efficient, perhaps due to displacement of the equilibria in the equations causing the formation of an active intermediate to be less likely to occur. Thus, the reaction may be made more efficient by using the system $[Rh(C_8H_{14})_2Cl]_2 \div 2\ PPh_3$, rather than $[RhCl(PPh_3)_3]$. The relative ratios of the isomers formed does not follow a regular sequence but there is a trend towards formation of an increasing proportion of II with a concomitant decrease in III, as the amount of triphenylphosphine added is increased.

TABLE 1

HYDROSILYLATION OF 1-PENTYNE CATALYZED BY TRIPHENYLPHOSPHINE-RHODIUM COMPLEXES [a]

Ratio of Ph_3P/Rh	Yield of pentenylsilanes [b]	Ratio of isomers I/II/III [c]
0	75	29/61/10
0.5	99	29/61/10
1.0	93	36/54/10
1.5	48	24/63/13
2.0	42	27/60/13
3.0	20	37/50/14
4.0	19	40/50/12

[a] 1-pentyne (10 mmol) and $HSiEt_3$ (6.3 mmol) added to $[RhCl(C_8H_{14})_2]_2$ 10 mg, 1.4×10^{-2} mmol) and PPh_3; heated at 60°C for 6 h. [b] Based on silane; calculated by GLC. [c] Estimated by GLC.

Effect of variation of phosphine

In order to obtain a better understanding of the reaction, ligands other than triphenylphosphine were used in conjunction with $[RhCl(C_8H_{14})_2]_2$, generating species such as L_nRhCl in situ. The results of these experiments are summarized in Table 2. The results may be readily interpreted. Schwartz [6] has proposed with supporting evidence, that addition of hydrides to acetylenes occurs in a *cis*-fashion only, followed by isomerization of the vinylmetal compound to the *trans*-adduct. This proposal is attractive as no reasonable mechanism has been proposed to explain trans-addition of a metal hydride to an acetylene. The mechanism, adapted to show hydrosilylation, is shown schematically in Scheme 1. Isomerization is proposed to occur via a dipolar intermediate, similar to that proposed for a ruthenium complex [7]. The ease of isomerization via this route would depend on stabilizing the dipolar intermediate, and this could be enhanced by ligand which are good donors. Thus this theory would predict that more of the *cis*-pentenylsilane II would be formed using ligands that were good donors, as these would stabilize the dipolar intermediate.

The proportion of II formed decreases in order $P(o\text{-}C_6H_4OMe)_3 >> PPh_3 \sim P(o\text{-}C_6H_4Me)_3 \sim P(p\text{-}C_6H_4OMe)_3 >> P(OMe)_3 \sim P(OEt)_3 \sim P(OPh)_3$. This exactly parallels the donor ability of the ligands as determined by Tolman for nickel carbonyl complexes [8]. This suggests that the mechanism of Schwartz is probably operating in this case. A second possibility is that isomerization is occurring, although this has been shown to be slow, with respect to hydrosilylation [3]. To confirm that this was the case under our conditions, we monitored the hydrosilylation of 1-pentyne by triethylsilane using triphenylphosphine as ligand for 126 h. After 6 h the reaction was

essentially complete and the ratio of I/II/III was 36/54/10, After 120 h longer at 60°C the ratio was 24/63/13. Thus isomerization is indeed slow compared to hydrosilylation and probably can be discounted under our experimental conditions.

TABLE 2

HYDROSILYLATION OF 1-PENTYNE BY TRIETHYLSILANE CATALYZED BY LIGAND-RHODIUM COMPLEXES [a]

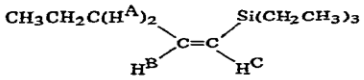
Ligand	Ratio of P/Rh	Yield of pentenylsilanes [b]	Ratio of I/II/III [c]
PPh_3	1.0	93	36/54/10
$P(p\text{-}C_6H_4OMe)_3$	1.0	86	43/56/10
$P(o\text{-}C_6H_4Me)_3$	1.0	57	35/54/11
$P(OMe)_3$	1.0	85	56/39/ 5
$P(OEt)_3$	1.0	87	58/36/ 5
$P(OPh)_3$	1.0	70	63/30/ 6
$P(o\text{-}C_6H_4OMe)_3$	1.0	82	9/82/ 9
$Ph_2PCH_2CH_2PPh_2$	0.5	60	31/56/12
$Ph_2PCH_2PPh_2$	0.5	76	30/61/12

[a] 1-Pentyne (10 mmol) and $HSiEt_3$ (6.3 mmol) added to $[RhCl(C_8H_{14})_2]_2$ (10 mg, 1.4×10^{-2} mmol) and ligand (2.8×10^{-2} mmol); heated at 60°C for 6 h. [b] Based on silane; calculated by quantitative GLC. [c] Estimated by GLC.

TABLE 3

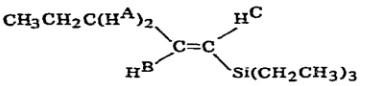
^1H NMR DATA FOR (I) AND (II) [c]

cis-1-Triethylsilyl-1-pentene



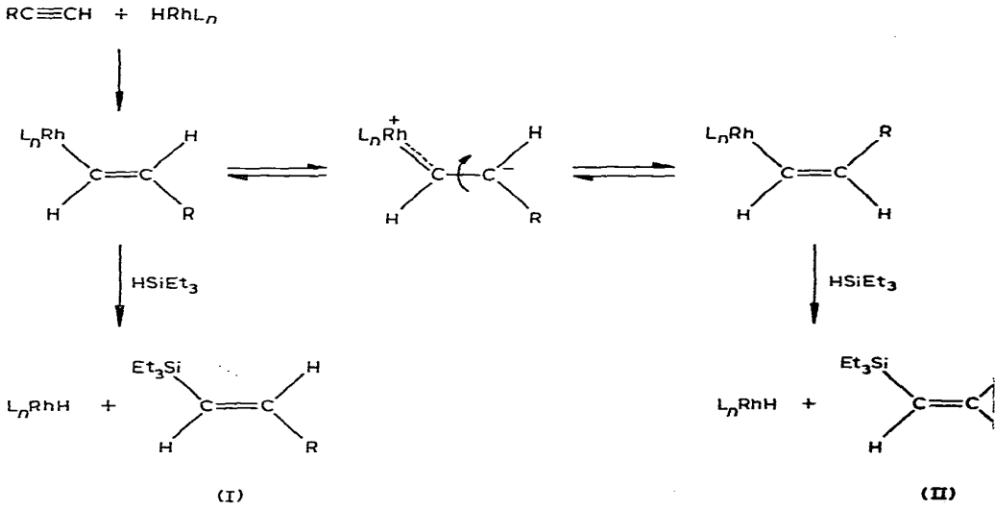
Chemical shift (τ, ppm)	Integration	Description	Assignment (Coupling constant)
3.77	1H	5 peaks (overlapping doublet of triplets)	H^B (J_{BC} = 13 Hz, J_{AB} = 6.5 Hz)
4.71	1H	Doublet	H^C (J_{BC} = 13 Hz)
7.8—8.2	2H	Multiplet	H^A
8.2—9.6	20H	Series of peaks	Si—CH_2—CH_3 and C=C—C—CH_2CH_3

trans-1-Triethylsilyl-1-pentene



Chemical shift (τ, ppm)	Integration	Description	Assignment (coupling constant)
4.00	1H	Doublet of triplets	H^B (J_{BC} = 18 Hz, J_{AB} = 6 Hz)
4.65	1H	Doublet	H^C (J_{BC} = 18 Hz)
7.7—8.2	2H	Multiplet	H^A
8.3—9.6	20H	Series of peaks	Si—CH_2—CH_3 and C=C—C—CH_2—CH_3

[a] 60 MHz spectra; CCl_4 solution: TMS reference.



SCHEME 1. Proposed mechanism for hydrosilylation of acetylenes.

Our experimental conditions differ from those where more extensive isomerization occurs [4], in that we have consistently used an excess of acetylene (ratio of 1-pentyne/triethylsilane 1.6/1). The excess 1-pentyne would be expected to compete favorably with the olefinic adduct, for the rhodium hydride species, believed to be the isomerization catalysts. This would yield the vinylrhodium intermediate, and not the hydride on completion of hydrosilylation.

Thus it seems that good donor ligands give II and good acceptor ligands give I. Steric effects seem to be unimportant as regards the relative ratio of the isomers formed, but increased steric bulk causes a decrease in overall chemical yield, the yield of pentenylsilanes dropping from 93% for PPh_3 to 57% for $P(o\text{-}C_6H_4Me)_3$. This decrease in yield is attributable to the greater steric bulk of $P(o\text{-}C_6H_4Me)_3$, as both ligands have similar donor properties [8]. The ratio of isomers is similar for both ligands (PPh_3, 36/54/10; $P(o\text{-}C_6H_4Me)_3$, 35/54/11), suggesting that the ratio is determined mainly by the donor ability of the ligands.

Experimental

General procedures

All reactions were carried out under pure nitrogen, using freshly distilled dry liquids. ^1H NMR spectra were recorded on a Varian Associates T60 spectrometer. Triethylsilane and 1-pentyne were commercial samples, dried over molecular sieves and distilled before use. Dichlorotetrakis(cyclooctene)dirhodium(I) was prepared according to the literature method [9].

Hydrosilylation of 1-pentyne by triethylsilane

(a) Preparative reactions. $[RhCl(C_8H_{14})_2]_2$ (0.10 g, 0.14 mmol) was placed in a flask fitted with a condenser and nitrogen inlet. Triphenylphosphine (73 mg, 0.28 mmol) was added to give a Rh/PPh_3 ratio of 1/1, followed by 1-pentyne (3.45 g, 50 mmol) and triethylsilane (3.65 g, 32 mmol) and the mixture was heated to 60°C for 6 h. After removal of volatiles under reduced pressure, vacuum distillation yielded 1-triethylsilyl-1-pentenes (5.1 g, 86% based on silane); b.p. 70°C/7 mmHg. Found: C, 71.4; H, 13.5. $C_{11}H_{24}Si$ calcd.: C, 71.7; H, 13.1%. The two major isomers were isolated by preparative GLC using a Varian Aerograph 700 "Autoprep" Gas Chromatograph using a 20' by 3/8" column of 15% SE30 on Chromosorb G at 200°C. They were identified as *cis*-and *trans*-1-triethylsilyl-1-pentene by their ^1H NMR spectra (Table 3).

(b) Quantitative reactions. These were carried out as above using $[RhCl(C_8H_{14})_2]_2$ (10 mg, 1.4×10^{-2} mmol), the appropriate amount of phosphine, 1-pentyne (0.69 g, 10 mmol) and triethylsilane (0.73 g, 6.3 mmol). The reaction mixture was heated at 60°C for 6 h and the yield and ratio of isomers determined by quantitative GLC on a Varian Aerograph 700 "Autoprep" Gas Chromatograph using a 6 ft. column of 10% FFAP on Chromosorb G using indan as an internal standard.

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