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## Platinum catalyzed hydrosilylation of alkynes: comparison of rates of addition of terminal olefins to internal alkynes

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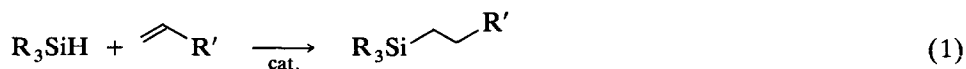
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### Abstract

The relative rates of platinum catalyzed hydrosilylation of terminal olefins *versus* internal alkynes were compared in competitive reactions.  $(\text{EtO})_3\text{SiH}$  added almost exclusively (97%) to  $\text{PhC}\equiv\text{CPh}$  *versus* styrene. The reaction of  $(\text{EtO})_3\text{SiH}$  with equimolar amounts of 2-decyne and 1-hexene gave a 78:22 ratio of alkyne products **6/6'** *versus* alkene product **7**. The reaction of  $(\text{EtO})_3\text{SiH}$  with equimolar amounts of styrene and 1-phenyl-1-propyne gave a 78:22 ratio of alkyne products **10/10'** to products **9**. The silane,  $\text{Me}_3\text{SiOSiMe}_2\text{H}$ , reacted with equimolar amounts of 2-decyne and 1-hexene to give a 90:10 ratio of alkyne products **8/8'** to alkene product **9**. All of the products had *E* stereochemistry about the C=C double bond as determined by  $^{29}\text{Si}$  NMR ( $^3J(\text{Si}-\text{H})$ ).

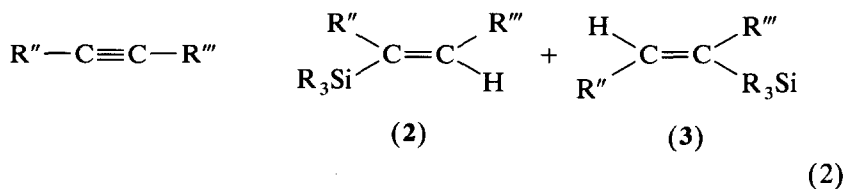
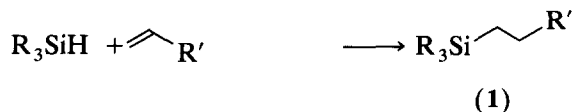
### Introduction

The hydrosilylation reaction, eq. 1, has received considerable attention over the years [1–7]. It remains one of the easiest ways to form a Si–C bond. In the course of hundreds of reports it is now well established that  $\text{R}_3\text{SiH}$  adds to terminal alkynes at a higher rate than to terminal olefins [1] and  $\text{R}_3\text{SiH}$  adds to terminal olefins at a higher rate than to internal olefins [4,6]. There are considerable industrial applications for vinyl and alkenyl substituted silicones in hydrosilylation. In principle, alkynyl silicones might replace alkenyls. For synthetic reasons, silicones with internal alkynes are easier to prepare than ones containing terminal alkynes. However, there is no clear trend with regard to the relative rates of addition of  $\text{R}_3\text{SiH}$  to internal alkynes *versus* terminal olefins.



This note describes a number of competitive experiments designed to determine which functional group is more reactive (eq. 2) towards addition of  $\text{R}_3\text{SiH}$ .

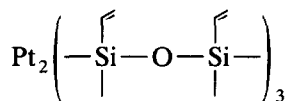
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In the course of this study the selectivity of 2 or 3 was noted during the alkyne hydrosilylation.

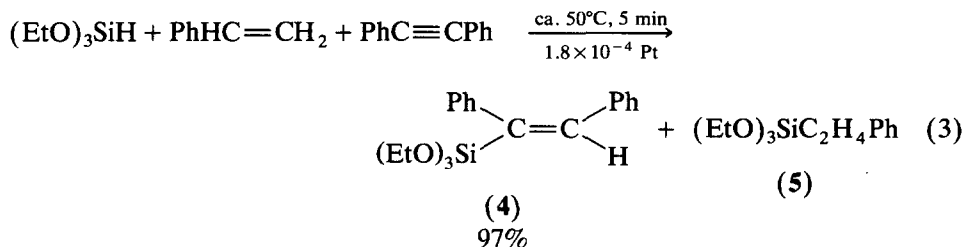
### Results and discussion

We wished to establish the relative rate of addition of  $\text{R}_3\text{SiH}$  to terminal alkenes *versus* internal alkynes. We endeavored to make the electronic environments on the olefin and alkyne as similar as possible. Unless stated otherwise, the highly active Karstedt Pt catalyst was employed in all cases [8,9].



#### Karstedt Pt Catalyst

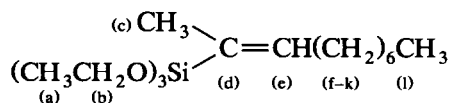
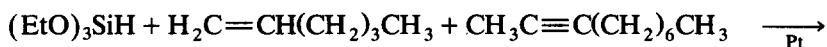
As shown in eq. 3, equimolar amounts of  $(\text{EtO})_3\text{SiH}$ ,  $\text{PhHC}=\text{CH}_2$  and  $\text{PhC}\equiv\text{CPh}$  were combined in the presence of 100 ppm Pt (or substrate/Pt molar ratio of  $1:1.8 \times 10^{-4}$ ) with gentle heating to initiate the reaction.



Product 4 was formed with the near total exclusion of any reaction product of  $(\text{EtO})_3\text{SiH}$  with styrene; about 3% of the reactive mixture contained styrene products, 5, as noted by gas chromatographic (GC) analysis. The  $(\text{EtO})_3\text{SiH}$ /styrene products have been reported previously [8]. Product 4 was also formed when the reaction in eq. 3 was carried out without styrene present and the structure of 4 was confirmed by  $^1\text{H}$  and  $^{13}\text{C}$  (attached proton test, APT) NMR, GC and elemental analysis.

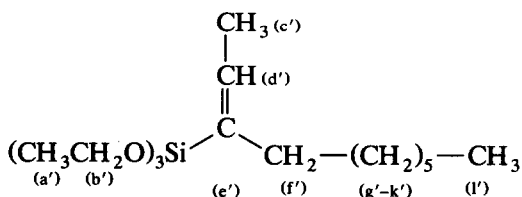
The relative rates of addition of  $(\text{EtO})_3\text{SiH}$  to 1-hexene *versus* 2-decyne were compared. Triethoxysilane addition to 1-hexene is known to be rapid and selective to give >98%  $\beta$  addition product [10], however, as shown in eq. 4,  $(\text{EtO})_3\text{SiH}$

added at a higher rate to the 2-alkyne as opposed to the terminal olefin.



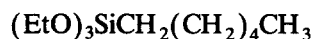
(6)

54%



(6')

24%



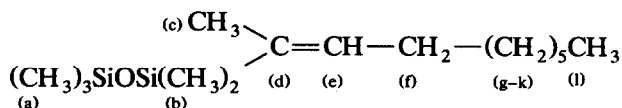
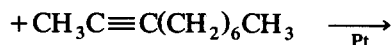
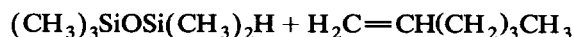
(7)

22%

(4)

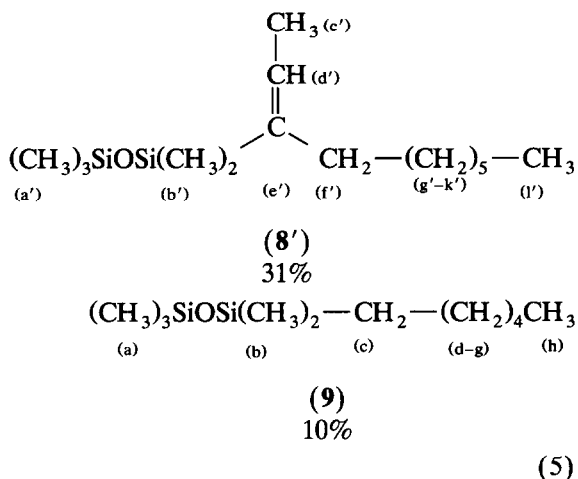
There was 78% total product based on alkyne addition (6 and 6') with 22% product based on alkene addition 7. The ratio of products was determined by GC and  $^1\text{H}$  NMR integration. Products 6/6' were separated from product 7 by vacuum distillation. The ratio of 6/6' was determined by integration of the methyne protons, quartet in 6' and triplet of quartets in 6. Structural assignments were further confirmed by  $^{13}\text{C}$  NMR (APT) and high resolution gas chromatography mass spectroscopy (HRGC-MS).

The relative rate of addition of  $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_2\text{H}$  to 1-hexene *versus* 2-decyne (eq. 5) was compared.  $(\text{CH}_3)_3\text{SiO}(\text{CH}_3)_2\text{H}$  was chosen because it closely represents the SiH encountered in an industrial silicone.



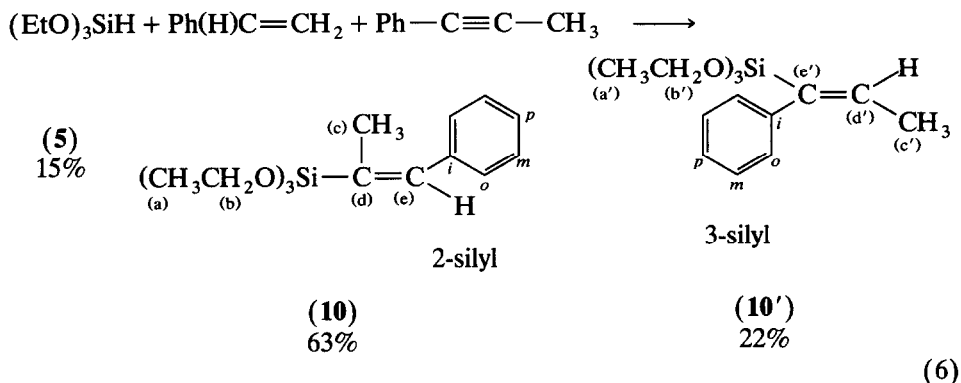
(8)

59%



The ratio of products in eq. (5), based on alkyne addition (**8** + **8'**) *versus* alkene addition (**9**), was 90:10. This ratio compared to the 78:22 ratio obtained for the similar reaction of eq. 5. The ratio of the two alkyne based addition products in eq. 4 was **8**/**8'** = 1.9, which compared to the ratio of **6**/**6'** = 2.25 from eq. 4. As in eq. 4, the ratio of **8**/**8'** in eq. 5 was determined by <sup>1</sup>H NMR integration of the methyne protons. The **8**/**8'** mixture was separated from **9** by distillation and all structural assignments were confirmed by <sup>1</sup>H and <sup>13</sup>C NMR (APT) and HRGC-MS.

As a final example, the relative rate of addition of (EtO)<sub>3</sub>SiH to styrene *versus* PhC≡CCH<sub>3</sub> was compared (eq. 6).



As with all of the previous examples, (EtO)<sub>3</sub>SiH added to the alkyne at a higher rate than to the olefin as determined by GC. A pure mixture of **10**/**10'** was separated from **5** by vacuum distillation. The overall ratio of **5**, **10**, **10'** were determined by GC and <sup>1</sup>H NMR integration.

The reactions of alkynes with (EtO)<sub>3</sub>SiH or Me<sub>3</sub>SiOSiMe<sub>2</sub>H gave mixed isomers in each case. It was not possible to separate these isomers in pure form but good separation by GC was achieved in each case. In addition, the <sup>1</sup>H and <sup>13</sup>C NMR resonances were well separated for the mixture of isomers. The absolute stereochemistry (*Z* *versus* *E*) was determined by <sup>29</sup>Si NMR with measurement of <sup>3</sup>J(Si-H).

The value of  $^3J(\text{Si-H})$  has been shown to be twice as high for the *transoid* 3 bond coupling as in  $\text{Si}-\text{C}=\text{C}-\text{H}$  versus the *cisoid* coupling constant in  $\text{Si}-\text{C}=\text{C}-\text{H}$  [11-14,15]. The *cisoid* arrangement of Si relative to H corresponds to the *E* isomer for all of the alkenyl products described here. NMR studies on closely related compounds to those reported here have  $^3J$  coupling constants for the *cisoid* arrangement versus *transoid* arrangement of 4-7 Hz versus 11-17 Hz [13-15]. The  $^{29}\text{Si}$  NMR spectra were recorded for **4**, **6,6'**, **8,8'** and **10,10'**. In all cases the spectra were recorded with the proper off resonance decoupling necessary to determine the  $^3J(\text{Si-H})$  coupling constants. In three cases (**6, 6'**; **8, 8'**; **10, 10'**), it was unequivocally determined that the *E* (not the *Z*) isomer was the only stereoisomer.

The  $^3J(\text{Si-H})$  coupling constant of from 3 to 6 Hz found for these compounds clearly fell within the range for a *cisoid* arrangement of Si and H about the  $\text{C}=\text{C}$ . For compound **4** it was not possible to decouple the phenyl resonances without affecting the C-H resonance. In the coupled  $^{29}\text{Si}$  NMR spectrum of **4**, a 3.66 Hz spacing was observed but this could not be unequivocally assigned to the  $^3J(\text{Si-H})$  in question.

The general trend observed with the four reactions described here was that silane addition proceeds at a higher rate to internal alkyne versus terminal olefin. The results were repeated as relative rate experiments. The reactions of the Si-H compounds with the alkynes alone proceeded to 100% completion at ambient temperature in 10-15 min. The corresponding reactions with 1-hexene or styrene were slow at room temperature. Qualitatively, the relative reactivities of alkyne versus alkene from eqs. 3-6 were verified as relative (instead of competitive) experiments. The addition of either  $(\text{EtO})_3\text{SiH}$  or  $\text{Me}_3\text{SiOSiMe}_2\text{H}$  to 1-hexene (eqs. 4 and 5) employing Karstedt type catalyst, is generally considered to be a rapid, exothermic reaction. Thus, the addition to internal alkynes must be considered to be a very rapid reaction indeed. All the reactions reported were clean, giving nearly 100% conversion to the described products. Finally, addition of the SiH compounds to internal alkynes favors the least substituted site as shown in eqs. 4 and 5.

## Experimental

### General procedures

Reactions were carried out in air in virgin glass vials. Care was taken to use Pt-only syringes (syringe only used for Pt catalysts) to introduce catalysts. The Pt catalyst used throughout, unless specified otherwise, was the Karstedt catalyst described previously. This solution was 5% by weight Pt and was added by microliter syringe: 1  $\mu\text{L}$  delivers 0.25  $\mu\text{mol}$  Pt or about 50  $\mu\text{g}$  Pt [8,9]. NMR spectra were recorded on a GE QE-300 instrument ( $^1\text{H}$  and  $^{13}\text{C}$ , 300.15 and 75.48 MHz respectively) in  $\text{CDCl}_3$ , 7.26 ppm lock signal, all shifts,  $\delta$ , relative to TMS = 0 internal standard. All  $^{13}\text{C}$  NMR spectra were rerun using the APT sequence with the orientation of  $\text{CH}_3$ , CH up and  $\text{CH}_2$  and C (quat) down.

$^{29}\text{Si}$  NMR spectra were obtained on a General Electric Omega 500 NMR spectrometer, operating with an observation frequency of 99.347 MHz. Complete proton decoupling was achieved using a Waltz-16 pulse sequence at 500 MHz.

$^3J(\text{Si}-\text{H})$  was measured by irradiating at the methyl proton frequencies to remove long range coupling, and observing residual proton coupling to Si. Both experiments were done using gated decoupling and a pulse delay of 30 s.

GC product analyses were carried out using a Hewlett Packard Model 5890 instrument coupled to a Model 3393 integrator. A 1.52 m OV 101 column was employed and a thermal conductivity detector was used. GC-MS analyses were performed using a Varian Model MAT 311A instrument at 70 eV (EI mode) resolution set at 850, 30 m long  $\times$  0.32 mm i.d. DB FSWOCT column. HRGC-MS spectra were recorded on a VG Analytical Model ZAB-2F gas chromatograph mass spectrometer, run in the accurate mass mode at 5500 resolution. High resolution electron impact mass spectra (HREI-MS) were recorded on a MAT 731 instrument at 10000 resolution at 80 eV.

### Equation 3

Equimolar amounts of  $(\text{EtO})_3\text{SiH}$  (1.84 g, 11.2 mmol),  $\text{PhC}\equiv\text{CPh}$  (2.00 g, 11.2 mmol) and  $\text{PhCH}=\text{CH}_2$  (1.17 g, 11.3 mmol) were combined with Karstedt catalyst (8  $\mu\text{L}$ , 2  $\mu\text{mol}$  Pt). The reaction was run at ambient temperature. Analysis by GC after 3 days showed  $>90\%$  conversion to products based on  $\text{PhC}\equiv\text{CPh}$ . The analytical data for the reaction products of  $(\text{EtO})_3\text{SiH}$  with  $\text{PhCH}=\text{CH}_2$  was the same as reported previously [8].

### Synthesis of 1,2-diphenyl-1-triethoxysilylethylene (4)

$(\text{EtO})_3\text{SiH}$  (9.19 g, 56 mmol) was combined with  $\text{PhC}\equiv\text{CPh}$  (10.09 g, 56 mmol) which was then heated to melting and then Karstedt catalyst (40  $\mu\text{L}$ , 10.4  $\mu\text{mol}$  Pt) was added. Analysis of the mixture by GC after 1 h showed complete conversion to product. The product was purified by distillation, 125 $^\circ$ -127 $^\circ\text{C}$ , 0.15 mmHg and 15.6 g (81% yield) of an oil was obtained. HRGC-MS calc. for  $\text{C}_{20}\text{H}_{26}\text{O}_3\text{Si}$  ( $M^+$ )  $m/e$  342.1651, found  $m/e$  342.1626. Anal. Found: C, 68.96; H, 7.49; Si, 7.80.  $\text{C}_{20}\text{H}_{26}\text{O}_3\text{Si}$  calc.: C, 70.14; H, 7.65; Si, 8.20%.

$^1\text{H}$  NMR: 1.19 (t, 3H,  $J = 7$  Hz,  $\text{CH}_3$ ), 3.83 (q,  $J = 7$  Hz,  $\text{CH}_2$ ), 7.07 (m) + 7.19 (m) (arom + b), 7.19 (m, arom). The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra agreed with those already reported [16].  $^{29}\text{Si}$  NMR: -61.3 ppm.

### Equation 4

Equimolar amounts of  $(\text{EtO})_3\text{SiH}$  (4.38 g, 26.7 mmol), 1-hexene (2.25 g, 26.8 mmol) and 2-decyne (3.71 g, 26.9 mmol) were combined and then Karstedt catalyst (10  $\mu\text{L}$ , 2.6  $\mu\text{mol}$  Pt) was added. After 1 h at 50 $^\circ\text{C}$  analysis by GC showed complete consumption of  $(\text{EtO})_3\text{SiH}$  and the presence of unreacted hexene. A 78:22 decenyl:hexyl product ratio was present. The products were separated by distillation (0.15 mmHg), hexyl product, 7 b.p. 62 $^\circ\text{C}$  and decenyl products, b.p. 95-97 $^\circ\text{C}$ , (6/6') 2:1 ratio of isomers. HRGC-MS for 7 calc. for  $\text{C}_{12}\text{H}_{28}\text{O}_3\text{Si}$  ( $M^+$ )  $m/e$  248.1807, found  $m/e$  248.1774; calc. for ( $M^+ - \text{OEt}$ )  $m/e$  203.1546, found  $m/e$  203.1482.

### Synthesis of decenyl products 6/6'

Equimolar amounts of  $(\text{EtO})_3\text{SiH}$  (4.38 g, 26.7 mmol) and 2-decyne (3.71 g, 26.9 mmol) were combined and then Karstedt catalyst (10  $\mu\text{L}$ , 2.6  $\mu\text{mol}$  Pt) was added. An exothermic reaction was noted after about 2 min. Analysis by GC showed

complete consumption of  $(\text{EtO})_3\text{SiH}$  and formation of 35% of an early retention time (RT) product and 65% of a late RT product. HRGC-MS calc. for  $\text{C}_{16}\text{H}_{34}\text{O}_3\text{Si}$  ( $M^+$ )  $m/e$  302.2276, found for high RT product  $m/e$  302.2306; calc. ( $M^+ - \text{OEt}$ )  $m/e$  257.2077, found for low RT product  $m/e$  257.1892.  $^1\text{H}$  NMR integration established a 2:1 ratio of 2-silyl/3-silyl (6/6').

$^1\text{H}$  NMR: 0.88 (overlapping triplets, f, f'), 1.23 (overlapping triplets, a, a') 1.25 (br), 1.70 (s), 1.72 (s), 2.13 (q,  $J = 7$  Hz) + 3.79, 3.80 (overlapping quartets b, b'), 6.11 (t of q,  $J = 2$  Hz, 7 Hz, e), 6.21 (q,  $J = 7$  Hz, d').  $^{13}\text{C}$  NMR: 14.24 (c'), 14.50 (c), 18.30 (a, a', l, l'), {22.77, 28.45, 28.91, 29.07, 29.32, 29.47, 29.53, 30.01, 31.98, 32.02} (f-k, f'-k'), 58.38 (b), 58.46 (b'), 127.17 (d), 134.25 (e'), 139.76 (d'), 146.12 (e).  $^{29}\text{Si}$  NMR: 6 - 53.50 ( $^3J(\text{Si-H}) = 3.7$  Hz), 6' - 53.7 ( $^3J(\text{Si-H}) = 5.55$  Hz).

### Equation 5

Equimolar amounts of  $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_2\text{H}$  (3.95 g mL, 26.7 mmol), 1-hexene (2.25 g, 26.8 mmol) and 2-decyne (3.71 g, 26.9 mmol) were combined with Karstedt catalyst (3  $\mu\text{L}$ , 0.8  $\mu\text{mol}$  Pt). An exothermic reaction occurred within about 2 min and complete conversion to products was noted within 1 h by GC. Analysis by GC showed a hexyl:decenyl product ratio (9:8/8') of 10:90. The products were separated by distillation (0.2 mmHg), hexyl product (9) b.p. 33°C, decenyl products (8/8') b.p. 75°C. HRGC-MS calc. for 9  $\text{C}_{11}\text{H}_{28}\text{OSi}_2$  ( $M^+$ )  $m/e$  232.1679, ( $M^+ - \text{CH}_3$ )  $m/e$  217.1443, found  $m/e$  217.1444.

$^1\text{H}$  NMR: 0.07 (s, 6H, 9), 0.09 (s, 9H, a), 0.54 (t, 2H, 8,  $J = \text{Hz}$ , c), 0.92 (t, 3H, h), 1.33 (br, 8H, d-g).  $^{13}\text{C}$  NMR {0.34, 1.96} (a,b), 14.15 (h), 18.40 (c), {22.65, 23.26, 31.67, 33.15} (d-g).

### Synthesis of decenyl products 8 / 8'

Equimolar amounts of  $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_2\text{H}$  (3.95 g, 26.7 mmol) and 2-decyne (2.25 g, 26.8 mmol) were combined with Karstedt catalyst (3  $\mu\text{L}$ , 0.8  $\mu\text{mol}$  Pt). An exothermic reaction occurred within about 2 min. Analysis by GC after 1 h showed complete conversion to products. Two peaks were present but they were not well resolved. HRGC-MS calc. for  $\text{C}_{15}\text{H}_{34}\text{OSi}_2$  ( $M^+$ )  $m/e$  286.2148, ( $M^+ - \text{CH}_3$ )  $m/e$  271.1912, found for low RT product  $m/e$  271.1919, found for high RT product  $m/e$  271.1868.

$^1\text{H}$  NMR: 0.12 (s, a), 0.15 (s, a'), 0.16 (s), 0.94 (t,  $J = 7$  Hz), 1.34 (br), 1.70 (q,  $J = 1$  Hz), 1.71 (d,  $J = 1$  Hz), 1.74 (s), 1.82 (t,  $J = 3$  Hz), 2.15 (m,  $J = 7$  Hz), 5.84 (t of q,  $J = 7$  Hz, 1.5 Hz, e), 5.95 (q of t,  $J = 7$  Hz, 1 Hz, d').  $^{13}\text{C}$  NMR: -0.23 (a'), 0.70 (b'), 1.93 (a), 1.96 (b), 13.77 ( $\text{CH}_3$  of 8 and 8'), 14.08 ( $\text{CH}_3$  of 8'), 14.12 ( $\text{CH}_3$  of 8), {22.28, 22.73, 29.28, 29.31, 29.45, 31.95} (f-k), {22.75, 28.75, 28.79, 29.34, 30.14, 32.00} (f'-k'), 134.39 (d'), 135.77 (e), 140.30 (d), 142.45 (e').  $^{29}\text{Si}$  NMR: 8 + 7.39 ( $\text{Si}_a$ ), - 2.64 ( $^3J(\text{Si-H}) = 3.6$  Hz,  $\text{Si}_b$ ); 8' + 7.24 ( $\text{Si}_a$ ), - 2.68 ( $^3J(\text{Si-H}) = 5.55$  Hz,  $\text{Si}_b$ ).

### Equation 6

Equimolar amounts of  $(\text{EtO})_3\text{SiH}$  (4.38 g, 26.6 mmol),  $\text{PhC}\equiv\text{CCH}_3$  (3.10 g, 26.7 mmol), and styrene (2.76 g, 26.5 mmol) were combined with Karstedt catalyst (5  $\mu\text{L}$ , 1.3  $\mu\text{mol}$  Pt) and approximately 80% conversion to products occurred after 3 h at ambient temperature as determined by GC. Analysis by GC showed 85:15 propenyl:styryl products [8] where the propenyl products were a 74:26 ratio of

2-silyl : 3-silyl products. The styryl based products were separated from the propenyl based products by distillation (0.2 mmHg). A forecut at 87–89°C contained a mixture of the styryl and propenyl products; a fraction collected at 93°C contained a mixture of the propenyl based products free of the styryl based ones. HRGC–MS for the propenyl based products (low and high RT products) calc. for  $C_{15}H_{24}O_3Si$  ( $M^+$ )  $m/e$  280.1494, found for low RT product  $m/e$  280.1486, found for high RT product  $m/e$  280.1476.

For **10**:  $^1H$  NMR: 1.27 (t, 9H,  $J = 7$  Hz, a), 2.00 (d, 3H,  $J = 1.4$  Hz, c), 3.88 (q, 6H,  $J = 7$  Hz, b), 7.08 (d, 1H,  $J = 1.4$  Hz, e).  $^{13}C$  NMR: 16.21 (c), 18.31 (a), 58.65 (b), 127.99 (*p*), 128.08 (*o*), 129.33 (*m*), 130.80 (*i*), 137.96 (e), 142.13 (d).  $^{29}Si$  NMR: –54.18 ( $^3J(Si-H) = 4.88$  Hz).

For **10'**:  $^1H$  NMR: 1.16 (t, 9H,  $J = 7$  Hz, a), 1.85 (d, 3H,  $J = 7$  Hz, c'), 3.77 (q, 6H,  $J = 7$  Hz, b'), 6.52 (q,  $J = 7$  Hz, d').  $^{13}C$  NMR: 15.89 (c'), 18.16 (a'), 58.41 (b'), 125.81 (*p*), 127.01 (*o*), 128.58 (*m*), 136.60 (*i*), 140.14 (e'), 141.72 (d').  $^{29}Si$  NMR: –57.23 ( $^3J(Si-H) = 4.88$  Hz).

## References

- 1 I. Ojima, in S. Patai and Z. Rappoport (Eds.), *The Chemistry of Organic Silicon Compounds*, Wiley, New York, 1989, p. 1479.
- 2 D.A. Armitage, in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), *Comprehensive Organometallic Chemistry*, Vol. 2, Pergamon Press, Oxford, 1982, p. 117.
- 3 J.L. Speier, *Adv. Organomet. Chem.*, 17 (1979) 407.
- 4 E. Lukevics, Z.V. Belyakova, M.G. Pomerantseva and M.G. Voronkov, in D. Seyferth (Ed.), *J. Organomet. Chem. Library*, Vol. 5, Elsevier, Amsterdam, 1977.
- 5 J.F. Harrod and A.J. Chalk, in I. Wender and P. Pino (Eds.), *Organic Synthesis Via Metal Carbonyls*, Wiley, New York, 1977, p. 673.
- 6 C. Eaborn, R.W. Bott, in A.G. MacDiarmid (Ed.), *The Bond to Carbon*, Vol. 1, Marcel Dekker, New York, 1968.
- 7 A.J. Chalk and J.F. Harrod, *J. Am. Chem. Soc.*, 87 (1965) 16.
- 8 L.N. Lewis, *J. Am. Chem. Soc.*, 112 (1990) 5998.
- 9 L.N. Lewis and N. Lewis, *J. Am. Chem. Soc.*, 106 (1986) 7228.
- 10 L.N. Lewis, R.J. Uriarte and N. Lewis, *J. Catalysis*, 127 (1991) 67.
- 11 S.S. Danyluk, *J. Am. Chem. Soc.*, 87 (1965) 2300.
- 12 M. Grignon-Dubois and M. Laguerre, *Organometallics*, 7 (1988) 1443.
- 13 E. Liepiņš, Yu. Goldberg, I. Iovel and E. Lukevics, *J. Organomet. Chem.*, 335 (1987) 301.
- 14 E. Liepiņš, I. Birgele, E. Lukevics, V.D. Sheludyakov and V.G. Lahtin, *J. Organomet. Chem.*, 385 (1990) 185.
- 15 E. Liepiņš, I. Birgele, P. Tomsons and E. Lukevics, *Magn. Reson. Chem.*, 23 (1985) 485.
- 16 M. Green, J.L. Spencer, F.G.A. Stone and C.A. Tsipis, *J. Chem. Soc., Dalton Trans.*, (1977) 1525.