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Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

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To cite this Article Saiki, Takeaki(2008) 'Effect of Ether on Regioselectivity in Hydrosilylation of 1,5-Hexadiene with Chlorohydrosilanes Catalyzed by Homogeneous Platinum Catalysts', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 183: 7, 1556 — 1563

To link to this Article: DOI: 10.1080/10426500701693388

URL: <http://dx.doi.org/10.1080/10426500701693388>

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Effect of Ether on Regioselectivity in Hydrosilylation of 1,5-Hexadiene with Chlorohydrosilanes Catalyzed by Homogeneous Platinum Catalysts

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Hydrosilylation of 1,5-hexadiene with chlorohydrosilanes catalyzed by homogeneous platinum catalyst to produce 5-hexenylchlorosilanes was studied. The presence of ether additives was highly effective in improving the regioselectivity and the yield. The formation of a double-bond rearrangement isomer, cis-, or trans-4-hexenylchlorosilanes, during the hydrosilylation was reduced drastically, as well.

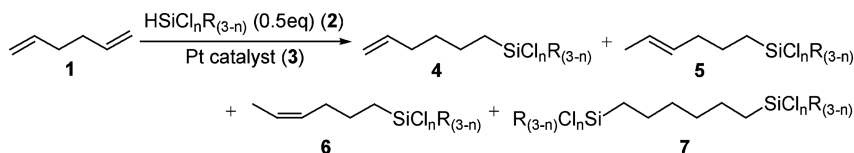
Keywords 1,5-hexadiene; ether; hydrosilylation; platinum; silicon

INTRODUCTION

Hydrosilylation of dienes is a versatile and efficient method for the synthesis of alkenylsilanes,^{1–4} which are important intermediates for organosilicon and silicone industries.^{5–7} However, hydrosilylation of 1,5-hexadiene with chlorohydrosilanes catalyzed by platinum compounds suffer from problems including poor regioselectivity and slow reaction rate. Although hydrosilylation of 1-hexene, 1,4-pentadiene, and 1,6-heptadiene gave a single isomer of *n*-hexylchlorosilanes, 4-pentenylchlorosilanes, and 6-heptenylchlorosilanes, respectively, in high yield, using 1,5-hexadiene gave a mixture of 5-hexenyl-, *trans*-4-hexenyl-, and *cis*-4-hexenyl-chlorosilanes in low yields as illustrated in Scheme 1. The use of heterogeneous platinum catalysts to achieve regioselective hydrosilylation of 1,5-hexadiene with chlorohydrosilanes has been reported with limited catalytic activity.⁸ In this paper, we report that specific ethers work well to afford 5-hexenylchlorosilanes regioselectively in the platinum catalyzed hydrosilylation of 1,5-hexadiene with chlorohydrosilanes.

Received 30 October 2006; accepted 20 August 2007.

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SCHEME 1 Hydrosilylation of 1,5-hexadiene with chlorohydrosilanes.

RESULTS AND DISCUSSION

The hydrosilylation of 1,5-hexadiene (25.0 mmol) with trichlorosilane (12.5 mmol) catalyzed by chloroplatinic acid (1.8×10^{-3} mmol) in *i*-PrOH (0.15 mmol)⁹ for 24 h at room temperature gave a mixture of 5-hexenyltrichlorosilane (**4**), *trans*-4-hexenyltrichlorosilane (**5**), *cis*-4-hexenyltrichlorosilane (**6**), and 1,6-bis(trichlorosilyl)hexane (**7**) in a total yield of 19%. The ratio of these products is shown in Table I, entry 1.

By adding an ether, polyethylene glycol, tetrahydrofuran, diethylene glycol dimethylether, or diethylene glycol dibutylether, the yield, as well as the selectivity, was drastically improved as listed in entries 2, 3, 4,

TABLE I Hydrosilylation of 1,5-hexadiene **1** with trichlorosilane **2a**.^a

$ \begin{array}{c} \text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O} (7.2 \times 10^{-5} \text{ mol}\%) \\ \text{additive} \\ (0.8 \text{ mol}\% \text{ of ether oxygen atom}) \\ \text{1} + \text{HSiCl}_3 \xrightarrow[\text{r.t./24 h}]{\text{(0.5 eq.)}} \text{4a} + \text{5a} + \text{6a} + \text{7a} \\ \text{(0.5 eq.)} \quad \text{SiCl}_3 \quad \text{SiCl}_3 \quad \text{SiCl}_3 \quad \text{SiCl}_3 \end{array} $				
Entry	Additive	Silane	4a:5a:6a:7a ^b	Yield [%] ^c
1	None	HSiCl ₃	48:39:13:0	19
2	Polyethylene glycol ^d	HSiCl ₃	89:9:0:2	99
3	Tetrahydrofuran	HSiCl ₃	89:10:0:1	99
4	Diethylene glycol dimethylether	HSiCl ₃	86:9:0:5	99
5	Diethylene glycol dibutylether	HSiCl ₃	85:9:0:6	99
6	1,4-Dioxane	HSiCl ₃	84:11:5:0	68
7	Ethylether	HSiCl ₃	84:10:6:0	48
8	Butylether	HSiCl ₃	81:11:8:0	40
9	<i>i</i> -Propylether	HSiCl ₃	69:25:6:0	34

^aA mixture of 1,5-hexadiene **1** (25 mmol), trichlorosilane **2a** (12.5 mmol), chloroplatinic acid (1.8×10^{-3} mmol) in 2-propylalcohol (0.15 mmol) and additives (0.2 mmol of ether oxygen atom) was stirred and allowed to stand at room temperature for 24 h. ^bThe isomer ratios were determined by GC and ¹H NMR. ^cGC yields based on trichlorosilane **2a**. ^dThe average molecular weight is 400.

and 5 in Table I. It should be noted that *cis*-4-hexenyltrichlorosilane (**6**) was completely absent (0%), when these additives were employed.

The addition of 1,4-dioxane exhibited slightly worse selectivity than the reaction using the above ethers with moderate yield (Table I, entry 6). The use of ethylether and butylether resulted in moderate selectivity with inferior yield (Table I, entries 7 and 8). Interestingly, the use of isopropylether was less effective in both regioselectivity and reactivity (Table I, entry 9). Diadduct 1,6-bis(trichlorosilyl)hexane (**7**) was not generated in the presence of 1,4-dioxane, ethylether, butylether, and isopropylether.

To extend the scope of the polyethylene glycol additive further, hydrosilylation of 1,5-hexadiene with chlorodimethylsilane or dichloromethylsilane was investigated (Table II). When dichloromethylsilane was used without any additives, lower selectivity with high yield was attained (Table II, entry 1). The addition of polyethylene glycol to the reaction mixture resulted in higher selectivity while keeping the high yield (Table II, entry 2). Hydrosilylation with chlorodimethylsilane showed higher selectivity with moderate yield without ether additives (Table II, entry 3). However, the addition

TABLE II Hydrosilylation of 1,5-Hexadiene 1 with Various Chlorohydrosilanes.^a

$ \begin{array}{c} \text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O} (7.2 \times 10^{-5} \text{ mol}\%) \\ \text{additive} \\ (0.8 \text{ mol}\% \text{ of ether oxygen atom}) \\ \text{1} + \text{HSiX}_3 \xrightarrow[\text{r.t./24 h}]{+} \text{CH}_2=\text{CH}(\text{CH}_2)_3\text{SiX}_3 \\ \text{(0.5 eq.)} \\ \text{2bX}_3 = \text{MeCl}_2 \\ \text{2cX}_3 = \text{Me}_2\text{Cl} \\ + \text{CH}_2=\text{CH}(\text{CH}_2)_3\text{SiX}_3 \quad \text{CH}_2=\text{CH}(\text{CH}_2)_3\text{SiX}_3 \quad \text{X}_3\text{Si}(\text{CH}_2)_6\text{SiX}_3 \\ \text{5b X}_3 = \text{MeCl}_2 \quad \text{6b X}_3 = \text{MeCl}_2 \quad \text{7b X}_3 = \text{MeCl}_2 \\ \text{5c X}_3 = \text{Me}_2\text{Cl} \quad \text{6c X}_3 = \text{Me}_2\text{Cl} \quad \text{7c X}_3 = \text{Me}_2\text{Cl} \end{array} $				
Entry	Additive	Silane	4b:5b:6b:7b ^b or 4c:5c:6c:7c ^b	Yield [%] ^c
1	None	MeHSiCl ₂	66:27:1:6	99
2	Polyethylene glycol ^d	MeHSiCl ₂	88:0:0:12	99
3	None	Me ₂ HSiCl	98:1:1:0	58
4	Polyethyleneglycol ^d	Me ₂ HSiCl	100:0:0:0	57

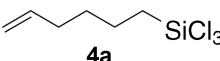
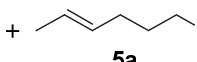
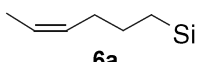
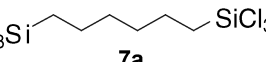
^aA mixture of 1,5-hexadiene **1** (25 mmol), chlorohydrosilane **2b** or **2c** (12.5 mmol), chloroplatinic acid (1.8×10^{-3} mmol) in 2-propylalcohol (0.15 mmol) and additives (0.2 mmol of ether oxygen atom) was stirred and allowed to stand at room temperature for 24 h. ^bThe isomer ratios were determined by GC and ¹H NMR. ^cGC yields based on chlorohydrosilane **2b** or **2c**. ^dThe average molecular weight is 400.

of polyethylene glycol to the hydrosilylation with chlorodimethylsilane had little effect on the selectivity and the yield (Table II, entry 4).

The effect of polyethylene glycol with various platinum catalysts was then examined with the results summarized in Table III. The hydrosilylation catalyzed by 1,3-divinyltetramethyldisiloxane-platinum complex^{10,11} exhibited low regioselectivity and moderate yield (Table III, entry 3). With the addition of polyethylene glycol, excellent regioselectivity and high yield were obtained (Table III, entry 4). The use of platinum on carbon as a heterogeneous catalyst gave excellent regioselectivity with very low yield (Table III, entry 5). The addition of polyethylene glycol to this reaction was slightly effective in increasing the yield (Table III, entry 6).

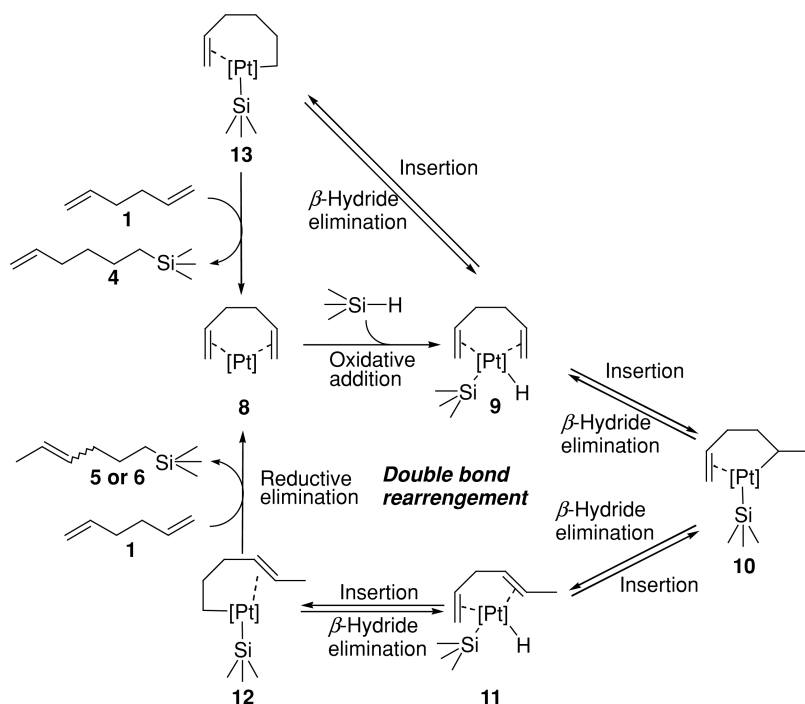
The effects of ethers were widely depended on the ether structures, chlorohydrosilanes, and the type of the platinum catalyst. The effectiveness of monoethers appeared to have increased with increasing coordinating ability. The excellent catalyst performance of multidentate ethers such as polyethylene glycol, diethylene glycol diethylether, and diethylene glycol dibutylether was probably a result of their strong multidentate coordination.

TABLE III Hydrosilylation of 1,5-Hexadiene **1 with Trichlorosilane **2a** Using Various Platinum Catalysts.^a**

Platinum catalyst (7.2×10^{-5} mol%) additive (0.8 mol% of ether oxygen atom) $1 + \text{HSiCl}_3 \xrightarrow[\text{r.t/24 h}]{(0.5 \text{ eq.})}$				
			 4a	
			 5a	
			 6a	
			 7a	
Entry	Additive	Catalyst	4a:5a:6a:7a^b	Yield [%] ^c
1	None	$\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in <i>i</i> -PrOH	48:39:13:0	19
2	Polyethylene glycol ^d	$\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in <i>i</i> -PrOH	89:9:0:2	99
3	None	$\text{Pt}_2 \left[\begin{array}{c} \diagup \quad \diagdown \\ \text{Si} \quad \text{O} \quad \text{Si} \\ \diagdown \quad \diagup \end{array} \right]_3$	75:22:3:0	63
4	Polyethylene glycol ^d	$\text{Pt}_2 \left[\begin{array}{c} \diagup \quad \diagdown \\ \text{Si} \quad \text{O} \quad \text{Si} \\ \diagdown \quad \diagup \end{array} \right]_3$	97:1:0:2	99
5	None	Pt/C (0.5%Ptw/w)	99:1:0:0	36
6	Polyethylene glycol ^d	Pt/C (0.5%Ptw/w)	100:0:0:0	50

^aA mixture of 1,5-hexadiene **1** (25 mmol), trichlorosilane **2a** (12.5 mmol), platinum catalyst (1.8×10^{-3} mmol) and additives (0.2 mmol of ether oxygen atom) was stirred and allowed to stand at room temperature for 24 h. ^bThe isomer ratios were determined by GC and ¹H NMR. ^cGC yields based on trichlorosilane **2a**. ^dThe average molecular weight is 400.

The widely accepted Chalk-Harrod mechanism for platinum-catalyzed hydrosilylation involves initial insertion of the olefin into the Pt-H bond followed by reductive elimination, forming a new Si-C bond.¹² Although we have not investigated the reaction mechanism yet, the double bond rearrangement may have proceeded through (a) generation of a (silyl)platinum 1,5-hexadiene complex (**9**) by oxidative addition of the Si-H bond to the platinum 1,5-hexadiene complex **8**, (b) anti-Markovnikov insertion of a double bond of 1,5-hexadiene to the Pt-H bond to form a 1-methyl-4-hexenylplatinum complex (**10**), (c) β -hydride elimination of the inner hydride to form a platinum 1,4-hexadiene complex (**11**) bearing a stable inner olefin, (d) insertion of the terminal double bond of 1,4-hexadiene to the Pt-H bond to form a 4-hexenylplatinum complex (**12**) and (e) coordination of 1,5-hexadiene (**1**) to **12** and reductive elimination of 4-hexenylsilanes (**5** or **6**) to regenerate a platinum 1,5-hexadiene complex **8** (see Scheme 2). We reasoned that ethers block coordination sites to prevent bidentate coordination of 1,5-hexadiene, and are suitable ligands of platinum compounds for the hydrosilylation of 1,5-hexadiene with chlorohydrosilanes exhibiting good catalytic performance.



SCHEME 2 Proposed double bond rearrangement mechanism.

In conclusion, we observed that platinum catalyzed hydrosilylation of 1,5-hexadiene with chlorohydrosilanes using ether additives gave high yield of 5-hexenylchlorosilanes as the major product. To our knowledge, this is the first observation that the presence of ether additives can change the product distribution in hydrosilylation and can improve the catalytic activity.

EXPERIMENTAL

All reagents were commercially available and were used as received. ^1H , ^{13}C , and ^{29}Si NMR spectra were recorded in CDCl_3 solutions using a JEOL JNM-EX400 spectrometer (400 or 100 MHz) with Me_4Si or residual protiated solvent as an internal standard. GC mass spectra were obtained on a Shimadzu GCMS-QP5050A operating at an ionization potential of 70 eV.

Catalytic Hydrosilylation of 1,5-Hexadiene—General Procedure

A glass tube containing 1,5-hexadiene (25 mmol) and an additive (0.2 mmol as ether oxygen atom) was stirred under nitrogen, followed by charging with a platinum catalyst (1.8×10^{-3} mmol) and a chlorohydrosilane (12.5 mmol). After sealing the tube with a screw cap, the mixture was stirred for 1 minute and allowed to stand at room temperature for 24 h. The product was isolated by distillation to give an analytically pure sample.

Hexenyltrichlorosilane (4a, 5a, 6a)¹³

The purity determined by NMR and GC analyses was >95%; b.p. 69°C/7 mmHg; ^1H NMR (δ 5-hexenyl isomer) 1.38–1.43 (m, 2H), 1.49–1.55 (m, 2H), 1.57–1.63 (m, 2H), 2.06–2.12 (m, 2H), 4.95–5.05 (m, 2H), 5.74–5.84 (m, 1H), (*trans*-4-hexenyl isomer) not assigned, (*cis*-4-hexenyl isomer) not assigned; ^{13}C NMR δ (5-hexenyl isomer) 21.72, 24.20, 30.98, 33.13, 115.03, 137.89, (*trans*-4-hexenyl isomer) 17.94, 22.18, 23.71, 34.48, 126.55, 129.60, (*cis*-4-hexenyl isomer) 12.87, 22.18, 23.80, 28.70, 125.45, 128.76; ^{29}Si NMR δ (5-hexenyl isomer) 12.91, (*trans*-4-hexenyl isomer) 13.14, (*cis*-4-hexenyl isomer) 13.04; GCMS (EI) m/z (%) (5-hexenyl isomer) 216 (M^+ , 1.6), 187 (2.5), 174 (17.6), 133 (22.4), 55 (100), (*trans*-4-hexenyl isomer) 216 (M^+ , 3.1), 187 (3.0), 174 (10.6), 133 (11.7), 55 (100), (*cis*-4-hexenyl isomer) 216 (M^+ , 4.0), 187 (5.5), 174 (13.0), 133 (15.1), 55 (100).

1,6-Bis(trichlorosilyl)hexane (7a)¹⁴

The purity determined by NMR and GC analyses was >95%; b.p. 149°C/10 mmHg; ¹H NMR δ 1.38–1.42 (m, 2H), 1.43–1.47 (m, 2H), 1.56–1.64 (m, 2H); ¹³C NMR δ 22.00, 24.17, 31.12; ²⁹Si NMR δ 12.84; GCMS (EI) *m/z* (%) 216 (12.4), 187 (24.0), 174 (49.6), 133 (81.6), 55 (100).

Hexenyldichloromethylsilane (4b, 5b, 6b)¹⁵

The purity determined by NMR and GC analyses was >95%; b.p. 65°C/5 mmHg; ¹H NMR (δ 5-hexenyl isomer) 0.75 (s, 3H), 1.08–1.14 (m, 2H), 1.46–1.57 (m, 4H), 2.05–2.10 (m, 2H), 4.94–5.03 (m, 2H), 5.73–5.83 (m, 1H), (*trans*-4-hexenyl isomer) not assigned, (*cis*-4-hexenyl isomer) not assigned; ¹³C NMR δ (5-hexenyl isomer) 5.18, 21.48, 21.89, 31.54, 33.25, 114.75, 138.30, (*trans*-4-hexenyl isomer) 5.18, 17.93, 21.05, 22.41, 35.07, 126.02, 130.19, (*cis*-4-hexenyl isomer) 5.18, 12.85, 21.15, 22.37, 29.27, 124.94, 129.37; ²⁹Si NMR δ (5-hexenyl isomer) 32.71, (*trans*-4-hexenyl isomer) 32.90, (*cis*-4-hexenyl isomer) 32.78; GCMS (EI) *m/z* (%) (5-hexenyl isomer) 196 (M⁺, 0.6), 181 (0.2), 167 (3.4), 154 (32.1), 113 (100), (*trans*-4-hexenyl isomer) 196 (M⁺, 10.0), 181(0.7), 167 (9.3), 154 (13.7), 141 (10.7), 113 (100), (*cis*-4-hexenyl isomer) 196 (M⁺, 8.0), 181 (1.4), 167 (8.7), 154 (12.8), 141 (9.2), 113 (100).

1,6-Bis(dichloromethylsilyl)hexane (7a)¹⁶

The purity determined by NMR and GC analyses was >95%; b.p. 128°C/5 mmHg; ¹H NMR δ 0.76 (s, 3H), 1.09–1.13 (m, 2H), 1.38–1.44 (m, 2H), 1.48–1.55 (m, 2H); ¹³C NMR δ 5.18, 21.49, 22.18, 31.74; ²⁹Si NMR δ 32.82; GCMS (EI) *m/z* (%) 295 (6.61), 197 (1.9), 154 (9.6), 141 (34.2), 113 (100).

Hexenylchlorodimethylsilane (4c¹⁷, 5c, 6c)

The purity determined by NMR and GC analyses was >95%; b.p. 73°C/7 mmHg; ¹H NMR δ (5-hexenyl isomer) 0.39 (s, 6H), 0.80–0.84 (m, 2H), 1.42–1.46 (m, 4H), 2.04–2.09 (m, 2H), 4.92–5.01 (m, 2H), 5.74–5.84 (m, 1H), (*trans*-4-hexenyl isomer) not assigned, (*cis*-4-hexenyl isomer) not assigned; ¹³C NMR δ (5-hexenyl isomer) 1.64, 18.85, 22.48, 32.17, 33.41, 114.47, 138.63, (*trans*-4-hexenyl isomer) not assigned, (*cis*-4-hexenyl isomer) not assigned; ²⁹Si NMR δ (5-hexenyl isomer) 31.61, (*trans*-4-hexenyl isomer) not assigned, (*cis*-4-hexenyl isomer) not assigned; GCMS (EI) *m/z* (%) (5-hexenyl isomer) 176 (M⁺, 0.1), 161 (0.4), 134 (18.2), 119 (4.2), 93 (100), (*trans*-4-hexenyl isomer) 176 (M⁺, 4.7) 148

(2.8), 134 (4.4), 121 (9.2), 93 (100), (*cis*-4-hexenyl isomer) 176 (M^+ , 5.5), 148 (2.5), 121 (10.9), 93 (100).

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