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# Rhodium-catalyzed transsilylation reactions between bis(trimethylsilyl)ethyne and hexyldimethylsilane

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## Abstract

Bis(trimethylsilyl)ethyne and hexyldimethylsilane undergo transsilylation reactions in the presence of Wilkinson's catalyst to give 1-hexyldimethylsilyl-2-trimethylsilylethyne and bis(hexyldimethylsilyl)ethyne. The reaction is faster in air than in argon but oxidation of the silane takes place which significantly reduces the yield.

## Introduction

We previously reported that a platinum-catalyzed reaction between bis(trimethylsilyl)ethyne (**1**) and hexyldimethylsilane (**2**) produces 1-hexyldimethylsilyl-2-trimethylsilylethyne (**3**), bis(hexyldimethylsilyl)ethyne (**4**) and various trisilylethenes in addition to the expected hydrosilylation product [1]. The formation of the disilylethynes is enhanced when oxygen is present in the atmosphere over the reaction mixture. It was proposed that a silyl-group exchange reaction (transsilylation reaction) takes place as a major reaction in the presence of oxygen, hydrosilylation being a minor one (Scheme 1).

Upon further investigation of the reactions of **1** and **2**, we have found that Wilkinson's catalyst [chlorotris(triphenylphosphine)rhodium(I)] catalyzes the transsilylation reaction with a high yield in an inert atmosphere. Only a trace amount of hydrosilylation product is formed either in the presence or absence of oxygen.

$$\underset{(\mathbf{1})}{Me_3SiC{\equiv}CSiMe_3} + \underset{(\mathbf{2})}{HexMe_2SiH} \xrightarrow{Pt}$$

$$\underset{(\mathbf{3})}{Me_3SiC{\equiv}CSiMe_2Hex} + \underset{(\mathbf{4})}{HexMe_2SiC{\equiv}CSiMe_2Hex} + Me_3SiH$$

(Hex = hexyl)

Scheme 1.

In this paper we report the transsilylation reactions catalyzed by rhodium. Also we report an oxidation reaction of hydrosilane catalyzed by rhodium which was found in the course of this investigation.

## Results and discussion

### *Transsilylation*

Bis(trimethylsilyl)ethyne (**1**) and hexyldimethylsilane (**2**) underwent transsilylation reactions in the presence of Wilkinson's catalyst to produce 1-hexyldimethylsilyl-2-trimethylsilylethyne (**3**) and bis(hexyldimethylsilyl)ethyne (**4**) under various conditions. The yields were determined by quantitative gas chromatography (GC) using tetradecane as an internal standard.

Preliminary experiments were performed in benzene at 75 ° C both in air and in argon. Figure 1 shows changes with time in the yields for the transsilylated products. It is shown that the reaction is faster in air than in argon but the reaction in air did not show further progress after the yield of **4** reached about 30% (4 h). Table 1 lists the principal products from the reaction in air for 24 h with their GC area percentages. The formation of hexylpentamethyldisiloxane (**5**) and 1,3-dihexyltetramethyldisiloxane (**6**) was confirmed by agreement of retention times and fragmentation patterns with authentic samples in GC-mass spectrometry (GC-MS). The structures of other minor products (**7**–**9**) were deduced from GC-MS and isomeric species cannot be ruled out.

Reactions producing the disiloxane compounds apparently consumed **2** to reduce the yields for intended products **3** and **4** as a result. As only a trace amount of

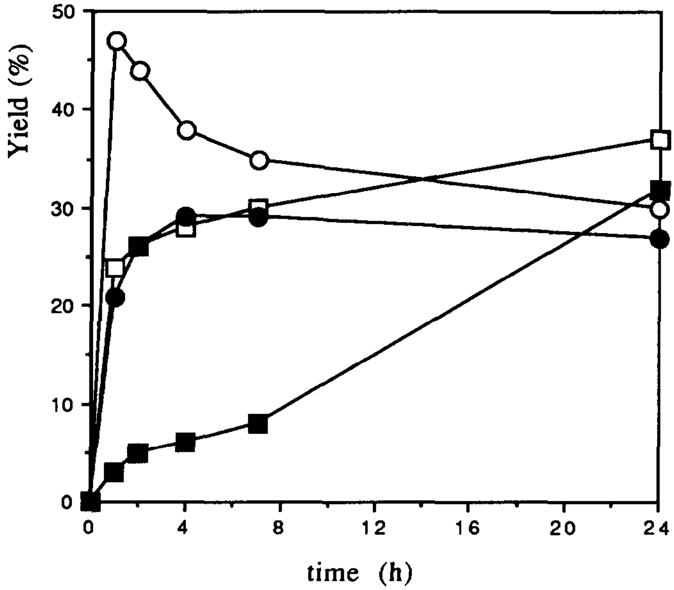
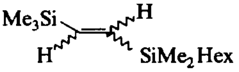
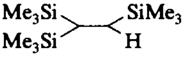


Fig. 1. Change in yields for transsilylated products with reaction time (75 ° C, in benzene, $[Rh]/[Me_3SiC{\equiv}CSiMe_3] = 0.018$). ○: 1-hexyldimethylsilyl-2-trimethylsilylethyne (**3**) in air, ●: bis(hexyldimethylsilyl)ethyne (**4**) in air, □: **3** in argon, ■: **4** in argon.

Table 1

Products from the reaction in air for 24 h (75 ° C)

| Product | GC area [a] |
|---|---|
| $Me_3SiC{\equiv}CSiMe_2Hex$ (3) [b] | 19.8 |
| $HexMe_2SiC{\equiv}CSiMe_2Hex$ (4) | 22.0 |
| $Me_3SiOSiMe_2Hex$ (5) | 17.7 |
| $HexMe_2SiOSiMe_2Hex$ (6) | 16.8 |
|  (7) | 2.5 |
|  (8) | 4.3 |
| $HexMe_2SiCH_2CH_2SiMe_2Hex$ (9) | 1.0 |

[a] Relative % area excluding solvent and internal standard, not calibrated. [b] Hex = hexyl.

byproduct 5 or 6 was detected from the reaction in argon, the formation of the disiloxanes can be attributed to reaction with oxygen. The most likely route is that 2 was oxidized catalytically to form a silanol compound, which then reacted with hydrosilanes (2 or $Me_3SiH$) to form the disiloxanes with evolution of hydrogen. The formation of hexyldimethylsilyl(trimethylsilyl)ethene (7) can be explained by hydrogenation of 3 by the hydrogen thus evolved. The latter part of this paper presents confirmation of the occurrence of the oxidation reaction.

Because oxygen has been found to cause side reactions to reduce yields, the detailed investigation was carried out using an argon atmosphere.

The results of reactions in argon are summarized in Table 2. It is shown that the reactions are slow but attain higher yields than those in air. The product mixture from run 1 contained trace amounts (less than 2% excluding the solvent and

Table 2

Transsilylation reactions in argon (75 ° C)

| Run | Solvent | Time (day) | [Rh]/[1 [a]] ($\times10^{-3}$) | [2 [b]]/[1] | Yield [c] (%) | |
|---|---|---|---|---|---|---|
| | | | | | 3 [d] | 4 [e] |
| 1 | benzene | 1 | 0.5 | 2.8 | 3.6 | 0.0 |
| 1 | | 3 | | | 45.7 | 43.1 |
| 1 | | 6 | | | 16.9 | 72.8 |
| 2 | benzene | 2 | 1.2 | 3.1 | 27.5 | 57.4 |
| 2 | | 6 | | | 3.0 | 77.7 |
| 3 | benzene | 1 | 2.8 | 2.6 | 35.0 | 49.3 |
| 3 | | 2 | | | 6.7 | 75.4 |
| 3 | | 3 | | | 4.9 | 69.6 |
| 4 | benzene | 1 | 22 | 3.0 | 28.0 | 6.3 |
| 4 | | 3 | | | 28.8 | 46.0 |
| 5 | DME [f] | 1 | 2.4 | 2.2 | 32.5 | 53.5 |
| 5 | | 4 | | | 18.4 | 61.3 |
| 6 | none | 1 | 2.7 | 2.3 | 21.8 | 54.7 |
| 6 | | 5 | | | 10.0 | 48.6 |

[a] Bis(trimethylsilyl)ethyne. [b] Hexyldimethylsilane. [c] Based on 1. [d] 1-Hexyldimethylsilyl-2-trimethylsilylethyne. [e] Bis(hexyldimethylsilyl)ethyne. [f] 1,2-Dimethoxyethane.

Table 3

Rh-catalyzed reaction of hexyldimethylsilane (**2**) in air (40 ° C) [a]

| Product | Time (h) | | |
|---|---|---|---|
| | 2 | 6 | 22 |
| $HexMe_2SiH$ | 37 | 15 | tr. |
| $HexMe_2SiOH$ | 38 | 40 | 40 |
| $(HexMe_2Si)_2O$ | 15 | 26 | 35 |

[a] GC area%, excluding peaks from solvent, not calibrated. $[Rh]/[HexMe_2SiH] = 6 \times 10^{-3}$.

tetradecane) of **5** and **6**, probably due to reaction with trace oxygen incorporated during the sampling procedures.

Comparison of runs 1–4 indicates that the reaction rate does not necessarily increase with the increased concentration of the catalyst. The rate is highest when the ratio of catalyst concentration to the concentration of **1** is $2.8 \times 10^{-3}$ (run 3). The reason for this phenomenon is not yet clear. Further kinetic study is needed.

The reaction in 1,2-dimethoxyethane (DME, run 5) proceeded in a similar fashion to that in benzene, showing that benzene is not the only solvent for the reaction.

The reaction was attempted in a mixture of benzene and dimethyl sulfoxide (DMSO, 5/1 w/w). The result was that hexyldimethylsilanol and **6** were formed as major products and only a trace amount of **3** was produced. Presumably most of hydrosilane **2** was quickly oxidized by DMSO before the reaction with **1**.

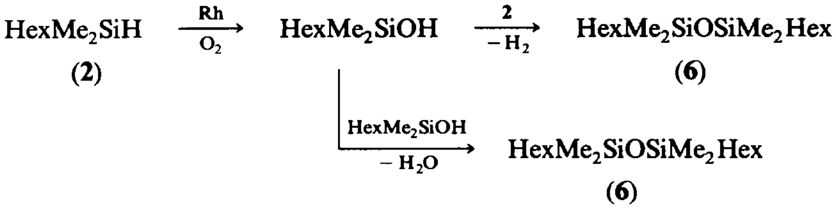
The reaction without solvent (run 6) gave **3** and **4** in relatively low yields. The cause for the reduced yield for **3** and **4** during the period of 1-day and 5-day reaction times (**3** + **4**: from 76.5 to 58.6%) is not clear, because no byproducts were detected by GC in corresponding amounts.

### *Oxidation of hydrosilane 2*

In order to confirm that hydrosilane **2** undergoes catalytic oxidation, **2** was mixed with the rhodium catalyst in toluene in dry air at 40 ° C. Rigorous precautions were taken to exclude humidity from the reaction system in order to prevent hydrolysis of the silane. The result is shown in Table 3 where each figure shows GC peak area percentage without calibration excluding the peak from the solvent. As shown, the silane was consumed quantitatively in 22 h. The major products are hexyldimethylsilanol and disiloxane **6**. The identification was made by agreement of retention times and fragmentation patterns in GC-MS with authentic samples. No detectable reaction took place when tris(tetramethyldivinyldisiloxane)diplatinum(0) [2] was used instead of the rhodium catalyst under the same conditions.

This result clearly shows that the silane underwent oxidation to give the silanol compound which, in turn, underwent condensation reactions either with the starting silane or with the silanol compound itself evolving hydrogen or water, respectively (Scheme 2). Water thus formed may react with **2** to give the silanol again via the well-known hydrolysis of SiH [3]. In Table 3, disiloxane **6** increased constantly with time whereas hexyldimethylsilanol remained at about 40%. This suggests that the self-condensation of silanol is not important in the present case.

Oxidation reactions of hydrosilanes by oxygen (at high temperatures) or ozone have been extensively investigated [4]. However, there have been few reports on



Scheme 2.

catalytic oxidation. Kuncova and Chvalovsky reported formation of disiloxane species from trialkylsilanes in the presence of Wilkinson's catalyst [5]. They did not detect silanol compounds and so they did not refer to intermediacy of silanols. Schubert et al. reported isolation of triphenylsilanol from a reaction of triphenylsilane in air in the presence of a heterogeneous rhodium catalyst obtained by a sol–gel process [6]. However, no sufficient analytical evidence for the silanol formation was described. Thus, to the best of our knowledge, this is the first clear evidence for non-hydrolytic formation of a silanol species from a hydrosilane under mild conditions by homogeneous rhodium catalysis.

In addition to the silanol and the disiloxane, at least nine minor products were detected by GC. According to GC-MS, they are hexane (GC area 10%) and di-, tri- or tetrasiloxane species which contain hexyl, methyl, hydroxy and SiH groups (GC area less than 4% each).

## Experimental section

### *Materials*

Bis(trimethylsilyl)ethyne (**1**), hexyldimethylsilane (**2**) [7] and solvents were distilled in argon and stored over activated molecular sieves. Tetradecane was stored likewise. Chlorosilanes were distilled in argon. Chlorotris(triphenylphosphine)rhodium(I) (Wilkinson's catalyst) was used as purchased.

### *Measurements*

GC analyses were performed with a Shimadzu GC-14AH gas chromatograph equipped with flame ionization detector and a CBM1 glass capillary column (0.1 μm thick, 25 m). Peak areas were determined with a Shimadzu C-R4A Chromatopac. GC-MS data were obtained using a Shimadzu GCMS-QP1000EX gas chromatograph-mass spectrometer. $^1$H and $^{29}$Si NMR spectra were recorded on either a Bruker AC-P 250 or a MSL 400 spectrometer [250.13 or 400.13 MHz for $^1$H; room temperature; solvent: $CDCl_3$; reference: $CHCl_3$ or $Me_4Si$ ($^1$H), $Me_4Si$ ($^{29}$Si)].

### *Transsilylation reactions*

The following shows a typical procedure. A double-necked 10-ml flask equipped with a reflux condenser was charged with Wilkinson's catalyst (amount shown in Table 2) and vacuum-dried with heating for 30 min. Benzene (3 ml), **1** (0.3 g, 1.76 mmol), **2** (amount shown in Table 2) and tetradecane (ca 0.2 g) were added and the mixture was degassed and purged with argon (high-purity grade) using a standard Schlenk line technique. The top of the reflux condenser was connected to a manifold with constant argon flow. The flask was then immersed in an oil bath at 75 °C with magnetic stirring for a specific period. The reaction was monitored by occasional sampling and analysis by GC. 1-Hexyldimethylsilyl-2-trimethylsilylethyne (**3**) and bis(hexyldimethylsilyl)ethyne (**4**) were isolated by preparative GC.

**3**: $^1$H NMR: $\delta$ 1.4–1.1 (m, 8H); 0.9 (t, 3H); 0.6 (t, 2H); 0.14 (s, 9H); 0.11 (s, 6H). $^{29}$Si NMR: $\delta$ $-17.2$ ($HexMe_2Si$); $-19.3$ ($Me_3Si$). MS: *m/e* (relative intensity, %) 225 (5) $M^+-$ Me; 155 (100) $M^+-$ hexyl; 152 (14); 141 (30); 73 (62) $Me_3Si$. Anal. Found: C, 64.52; H, 11.68. $C_{13}H_{28}Si_2$ calcd.: C, 64.91; H, 11.73%.

**4**: $^1$H NMR: $\delta$ 1.4–1.1 (m, 16H); 0.9 (t, 6H); 0.6 (t, 4H); 0.12 (s, 12H). $^{29}$Si NMR: $\delta$ $-17.2$ ($HexMe_2Si$). MS: *m/e* 295 (1.1) $M^+-$ Me; 225 (46) $M^+-$ hexyl; 152 (25); 143 (50); 141 (100); 127 (25); 125 (11); 99 (12); 83 (14); 73 (88). Anal. Found: C, 69.47; H, 12.23. $C_{18}H_{38}Si_2$ calcd.: C, 69.59; H, 12.33%.

### *Oxidation of hydrosilane 2*

A 10-ml flask equipped with a reflux condenser, whose top was connected to a $CaCl_2$ drying tube (15 mm i.d. × 300 mm), was charged with Wilkinson's catalyst (26 mg, 28 $\mu$mol) and vacuum-dried with heating. Air was admitted into the flask slowly through the drying tube. Toluene (10 ml) and **2** (0.7 g, 4.9 mmol) were added and the flask was immersed in an oil bath at 40 °C. The reaction was monitored in a similar manner to that above.

### *Preparation of authentic samples*

Hexyldimethylsilanol was prepared from hexyldimethylchlorosilane in diethyl ether and aqueous $NaHCO_3$ solution following the literature procedure [8]. Pure silanol was not isolated due to its instability to heat. A reaction of hexyldimethylsilanol (ca 5 g, 30 mmol) with chlorotrimethylsilane (3.5 g, 32 mmol) in the presence of triethylamine in diethyl ether at 0 °C gave hexylpentamethyldisiloxane (**5**). 1,3-Dihexyltetramethyldisiloxane (**6**) was obtained similarly from silanol and hexyldimethylchlorosilane.

Hexyldimethylsilanol: MS: *m/e* 160 (0.9) $M^+$; 145 (64) $M^+-$ Me; 127 (18); 75 (100) $M^+-$ hexyl; 61 (90).

**5**: b.p. 94–95 °C/30 Torr. $n_D^{25}$ 1.4090. $^1$H NMR: $\delta$ 1.4–1.2 (m, 8H); 0.9 (t, 3H); 0.5 (t, 2H); 0.06 (s, 9H); 0.03 (s, 6H). $^{29}$Si NMR: $\delta$ 7.55, 6.90. MS: *m/e* 217 (11) $M^+-$ Me; 147 (100) $M^+-$ hexyl; 133 (96); 119 (8); 117 (10); 73 (30) $Me_3Si$. Anal. Found: C, 56.41; H, 12.50. $C_{11}H_{28}Si_2O$ calcd.: C, 56.82; H, 12.14%.

**6**: b.p. 100–101 °C/0.8 Torr (lit. [9] 104–106 °C/3 Torr). $n_D^{25}$ 1.4262 (lit. [10] 1.4265). $^1$H NMR: $\delta$ 1.4–1.2 (m, 16H); 0.9 (t, 6H); 0.5 (t, 4H); 0.03 (s, 12H). $^{29}$Si NMR: $\delta$ 7.21. MS: *m/e* 287 (1.5) $M^+-$ Me; 217 (20) $M^+-$ hexyl; 133 (100); 119 (21); 117 (5); 73 (8).

### *GC-MS data for the compounds in Table 1*

**7**: *m/e* 157 (24) $M^+-$ hexyl; 143 (17); 142 (5); 73 (100) $Me_3Si$. **8**: *m/e* 244 (4) $M^+$; 159 (20); 143 (37); 85 (33); 73 (100) $Me_3Si$. **9**: *m/e* 297 (0.9) $M^+-$ Me; 227 (5) $M^+-$ hexyl; 143 (99); 73 (39); 59 (100).

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