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The synthesis of (*E*)-1,2-disilylethenes from a triorganosilylethene with the aid of $Ru_3(CO)_{12}$ and a hydrosilane

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Abstract

The $Ru_3(CO)_{12}$-catalyzed reaction of trimethylsilylethene with triethylsilane gives a mixture of (*E*)-1,2-bis(trimethylsilyl)ethene and (*E*)-1-triethylsilyl-2-trimethylsilylethene. The yield of (*E*)-1,2-bis(trimethylsilyl)ethene increases with an increase in the molar ratio of trimethylsilylethene to triethylsilane. The $Ru_3(CO)_{12}$-catalyzed reaction of trimethylsilylethene in the presence of a catalytic amount of triphenylsilane also gives (*E*)-1,2-bis(trimethylsilyl)ethene in good yields. Triorganosilylethenes such as dimethyl(ethoxy)silylethene and triethoxysilylethene also give the corresponding (*E*)-1,2-disilylethenes. The similar, catalyzed reaction of styrene with trimethylsilylethene gives 1-trimethylsilyl-2-phenylethene in good yields.

Introduction

1,2-Bis(trimethylsilyl)ethene has recently been shown to be a versatile intermediate in organic synthesis [1]. Several methods are available for the synthesis of 1,2-bis(trimethylsilyl)ethene, including the methods in which 1,2-bis(tributylstannyl)ethene [2] or trimethyl(diiodomethyl)silane [3] are used as the starting materials, hydrosilylation of trimethylsilylacetylene with dimethylchlorosilane [4], the reaction of trimethylsilylethene with trimethylchlorosilane and magnesium in the presence of titanium tetrachloride [5]. In these methods, chlorosilanes and hydrosilanes are mainly used as the silylating agents. However, up to now the use of triorganosilylethenes as silylating agents has received little attention.

During the course of our studies on the $Ru_3(CO)_{12}$-catalyzed reaction of alkenes with hydrosilanes [6], we have found that the reaction of trimethylsilylethene with triethylsilane gives 1,2-bis(trimethylsilyl)ethene as a byproduct. In this reaction, trimethylsilylethene plays the role of a silylating agent. Moreover, this reaction is of interest in connection with elucidating the mechanism of the hydrosilylation of

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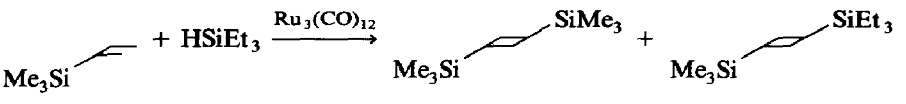
alkenes. We describe here the full details of the scope and the limitations of the activity of triorganosilylethenes as silylating agents.

Results and discussion

$Ru_3(CO)_{12}$-catalyzed reaction of trimethylsilylethene with triethylsilane

It has previously been reported that the $Ru_3(CO)_{12}$-catalyzed reaction of alkenes with hydrosilanes gives the corresponding 1-alkenylsilanes, which are dehydrogenative silylation products [6] (eq. 1). Similarly the reaction of trimethylsilyl-ethene with triethylsilane yields a mixture of (*E*)-1,2-bis(trimethylsilyl)ethene (**1a**) and (*E*)-1-triethylsilyl-2-trimethylsilylethene (**2**) (eq. 2). The results under various reaction conditions are shown in Table 1. With an excess of triethylsilane, **2** was mainly obtained in 79% yield based on trimethylsilylethene, along with **1a** in 19% yield. Interestingly, the yield of **1a** increased with an increase in the molar ratio of trimethylsilylethene. When a 2-fold excess of trimethylsilylethene was used, **1a** and **2** were produced in 37% and 59% yields, respectively. In the presence of a catalytic amount (0.5 mmol) of triethylsilane, the reaction proceeded with the evolution of ethylene and 1,2-bis(trimethylsilyl)ethene (**1a**) was obtained in 42% yield. On the other hand, in the absence of triethylsilane, the yield of **1a** was only 8%. These results suggest that a catalytic amount of triethylsilane is responsible for the formation of **1a**.

$$RCH{=}CH_2 + HSiR'_3 \xrightarrow{Ru_3(CO)_{12}} RCH{=}CHSiR'_3 + RCH_2CH_3 \qquad (1)$$



(2)

(**1a**) (**2**)

It is known that the $Ru_3(CO)_{12}$-catalyzed reaction of a 2-fold excess of styrene with triethylsilane gives almost quantitatively 1-triethylsilyl-2-phenylethene which is the corresponding dehydrogenative silylation product, along with ethylbenzene [6]. Therefore, in the present reaction, two types of reaction probably occur competitively: (i) dehydrogenative silylation of trimethylsilylethene with triethylsilane (eq.

Table 1

$Ru_3(CO)_{12}$-catalyzed reaction of $Me_3SiCH{=}CH_2$ with $HSiEt_3$ [a]

$Me_3SiCH{=}CH_2$ (mmol)	$HSiEt_3$ (mmol)	Yield (%) [b]	
		1a	**2**
20	50	9	79
20	20	25	67
20	10	37	59
20	4	47	61 [c]
20	0.5	42	56 [c]
20	–	8	–

[a] Reaction conditions; $Ru_3(CO)_{12}$ (0.05 mmol), 70 °C, 4 h, in benzene (10 ml). [b] Based on $Me_3SiCH{=}CH_2$ unless otherwise noted. [c] Based on $HSiEt_3$.

Table 2

Disproportionation of $Me_3SiCH{=}CH_2$ by $Ru_3(CO)_{12}$ and hydrosilanes [a]

Hydrosilane	Yield of **1a** (%)
$HSiEt_3$	42
$HSi(OEt)_3$	70
H_2SiPh_2	67
$HSiPh_3$	75
$HSiMe_2Ph$	67

[a] Reaction conditions; $Me_3SiCH{=}CH_2$ (10 mmol), $Ru_3(CO)_{12}$ (0.05 mmol), hydrosilane (0.5 mmol), 80 °C, 4 h in benzene (5 ml).

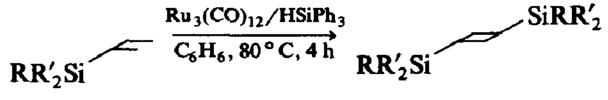
1), and (ii) disproportionation of trimethylsilylethene (eq. 3).

$$2\,Me_3SiCH{=}CH_2 \xrightarrow{\text{cat.}} \mathbf{1a} + CH_2{=}CH_2 \qquad (3)$$

Synthesis of various (E)-1,2-bissilylethenes

The catalytic activity of various hydrosilanes for the formation of **1a** from trimethylsilylethene (eq. 3) has been examined. The results are shown in Table 2. All hydrosilanes employed showed the catalytic activity for the formation of **1a**. In particular, hydrosilanes containing a phenyl group and triethoxysilane give **1a** in good yields. These hydrosilanes are less reactive to the dehydrogenative silylation reaction of alkenes (eq. 1). When triphenylsilane is used, pure **1a** is obtained readily by direct distillation, since triphenylsilane did not yield the corresponding dehydrogenative silylation product and the by-product was only ethylene which was liberated from the reaction mixture. Thus, the present reaction in the presence of a catalytic amount of triphenylsilane provides a convenient route to the 1,2-bissilylethenes (**1**).

The reaction of various triorganosilylethenes in the presence of a catalytic amount of $Ru_3(CO)_{12}$ and triphenylsilane has been examined. The reactions of dimethyl(ethoxy)silylethene and triethoxysilylethene also give the relevant products in 91% and 25% yields, respectively (eq. 4). On the other hand, the reaction of diphenylmethylsilylethene and dichloromethylsilylethene did not give the desired products. The results are shown in Table 3. Similar reaction of triethoxysilylethene under more forcing conditions, such as 140 °C for 5 hours without solvent, gives **1c** in only 16% yield. Recently, some Ru^{II} complexes have been shown to be effective only as the catalyst for the conversion of a trialkoxysilylethene into a 1,2-bis(trialkoxysilyl)ethene [7].



(4)

(**1a**: R = Me, R′ = Me;
1b: R = OEt, R′ = Me;
1c: R = OEt, R′ = OEt)

It is well known that transition metal complexes react with hydrosilanes to give oxidative addition products containing H–M and Si–M bonds [8] (eq. 5). However, it is not clear whether the ruthenium complex is

$$Ru_3(CO)_{12} + HSiPh_3 \longrightarrow H{-}(Ru){-}SiPh_3 \qquad (5)$$

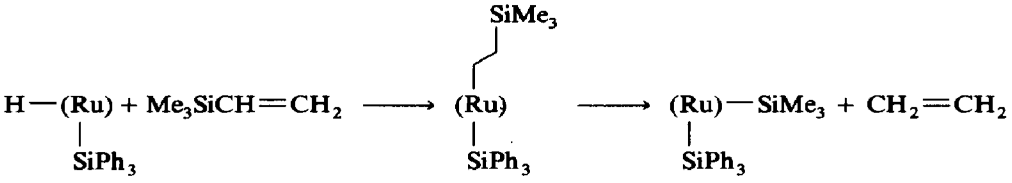
Table 3

Reaction of various triorganosilylethenes [a]

Triorganosilylethene	Yield of **1** (%)
$Me_3SiCH{=}CH_2$	76
$Me_2(EtO)SiCH{=}CH_2$	91
$(EtO)_3SiCH{=}CH_2$	25
$MePh_2SiCH{=}CH_2$	0
$Cl_2MeSiCH{=}CH_2$	0

[a] Reaction conditions: triorganosilylethene (20 mmol), $Ru_3(CO)_{12}$ (0.05 mmol), triphenylsilane (0.5 mmol), 80 °C, 2 h, in benzene (10 ml).

monomeric, dinuclear, or trinuclear. The insertion of alkenes into M–H bonds is well documented [9]. Therefore, the hydrido ruthenium complex should also react with trimethylsilylethene to give a β-trimethylsilylalkyl ruthenium complex (**3**). Recently, Wrighton and co-workers have reported that both β-H and β-$SiMe_3$ transfer occur competitively under near-UV irradiation of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2CH_2SiMe_3$ to form $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$, free ethylene, and $Me_3SiCH{=}CH_2$ [10]. It is reasonable to assume that the free ethylene arises from a β-$SiMe_3$ transfer in a β-trimethylsilyl ruthenium complex (**3**) (eq. 6).



$$\underset{\textstyle SiPh_3}{H{-}(Ru)} + Me_3SiCH{=}CH_2 \longrightarrow \underset{\textstyle SiPh_3}{\overset{\textstyle SiMe_3}{(Ru)}} \longrightarrow \underset{\textstyle SiPh_3}{(Ru)}{-}SiMe_3 + CH_2{=}CH_2$$

(**3**)

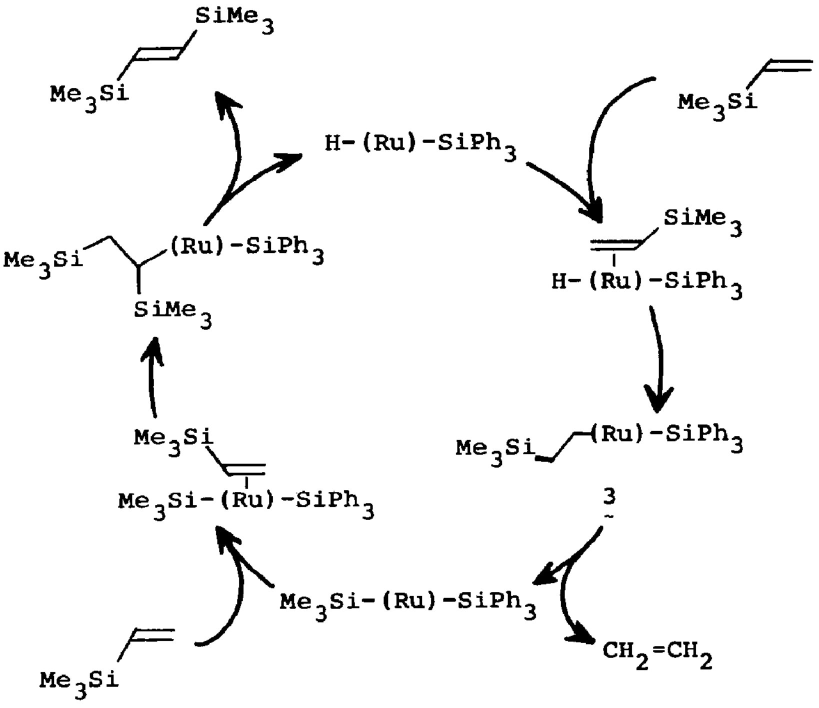
(6)

As to the formation of alkenylsilanes in the catalyzed reaction of alkenes with hydrosilanes, it has recently been proposed that the key steps of this mechanism are the insertion of an alkene into a M–Si bond followed by hydrido elimination [10,11]. Although no information relating to the mechanism of our present reaction is available, it is attractive to assume the similar reaction path as shown in Scheme 1.

The catalyzed reaction of a mixture of various alkenes and trimethylsilylethene

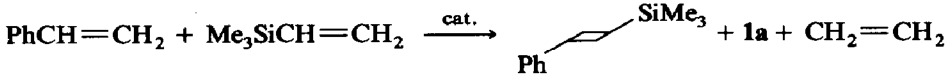
As mentioned above, trimethylsilylethene has been shown to act as a silylating agent. In the catalyzed reaction of alkenes with hydrosilanes, the hydrogenated and hydrosilylated products of alkenes have been known to be obtained together with 1-alkenylsilanes [11]. However, the present reaction is simple and gives only ethylene as a by-product. Thus, it is interesting to see whether trimethylsilylethene can silylate other alkenes.

A solution of styrene (10 mmol), trimethylsilylethene (20 mmol), $Ru_3(CO)_{12}$ (0.05 mmol), triphenylsilane (0.5 mmol), and benzene (10 ml) was heated at 80 °C for 7 h with stirring. The evolution of ethylene occurred slowly and the 1-Alkenylsilane, (*E*)-1-trimethylsilyl-2-phenylethene (**4**), was obtained in 59% yield based on



Scheme 1

styrene, along with **1a** in 60% yield based on trimethylsilylethene (eq. 7).



$$PhCH{=}CH_2 + Me_3SiCH{=}CH_2 \xrightarrow{cat.} PhCH{=}CHSiMe_3 + \mathbf{1a} + CH_2{=}CH_2 \qquad (7)$$

(4)

About 40% of the styrene was recovered unchanged. Therefore, the yield of **4** based on styrene consumed was almost quantitative. It has been reported that the $Ru_3(CO)_{12}$-catalyzed reaction of an excess amount of styrene with trimethylsilane gave **4** in high yield based on trimethylsilane [6]. However, in this case, the yield of **4** based on styrene was low, because styrene was consumed as the hydrogen acceptor to give ethylbenzene. No stilbene was formed (GLC).

Similarly, reaction of allylbenzene did not give the corresponding 1-alkenylsilanes. Nearly all the allylbenzene was isomerized to β-methylstyrene. When alkenes having hydrogen at the allylic position were used, isomerization of the alkenes occurred predominantly and consequently, only **1a** was obtained as the silylated product. The reaction of 1-hexene did not give the silylated product either. Therefore, this method in which trimethylsilylethene is used as the silylating agent is not useful for alkenes having a hydrogen at the allylic position.

The mechanism for the homogeneous catalysis of hydrosilylation as expounded by Chalk and Harrod has been accepted as a consistently useful theory [12], which has the key steps of (i) insertion of an alkene into the M–H bond of an Si–M–H complex, followed by (ii) the reductive elimination of the alkyl and the silyl groups to give an alkylsilane. In contrast, in our present reaction, both the trimethylsilyl ruthenium and hydrido ruthenium complexes are the key catalysts. This suggests the possibility that the insertion of an alkene into the M–Si bond of an Si–M–H complex is one of the key steps in the hydrosilylation of alkenes.

Hydrosilanes and chlorosilanes are used as silylating reagents in most of the procedures to make transition metal complexes containing an Si–M bond [8]. The present reaction provides a new route to complexes containing an Si–Ru bond.

Work is in progress to further examine the chemical reactivity of the triorganosilyl ruthenium intermediates.

Experimental

General comments

All temperatures are uncorrected. IR spectra were recorded with a Shimazu IR-435. The ^{1}H NMR spectra were measured on a Hitachi R-24B spectrometer with Me_4Si as an internal standard. Mass spectra were recorded on a JEOL JMS-DX303HF mass spectrometer. Analytical gas chromatography (GLC) was carried out by use of Shimazu GC-3BF with flame ionization detectors. Preparative GLC was carried out by use of a Hitachi GC-164. Hydrosilanes, triorganosilylethenes, and alkenes were commercial products. Benzene was dried over sodium-lead alloy. $Ru_3(CO)_{12}$ was a commercial product.

Reaction of triorganosilylethenes with a hydrosilane in the presence of a catalytic amount of $Ru_3(CO)_{12}$

A general procedure is given for the reaction of trimethylsilylethene in the presence of $Ru_3(CO)_{12}$ and triphenylsilane.

A 20-ml two-necked flask equipped with a reflux condenser, a rubber septum cap, and a magnetic stir bar was flame dried in a flow of nitrogen and then charged with 20 mmol of trimethylsilylethene, 0.05 mmol of $Ru_3(CO)_{12}$, 0.5 mmol of triphenylsilane, and 10 ml of benzene. The reaction vessel was evacuated and refilled to atmospheric pressure with pure nitrogen. This procedure was repeated three times. The solution was heated at 80 °C for 4 h with stirring. The evolution of ethylene occurred slowly. Analysis of the reaction mixture by GLC (a 6 m × 3 mm glass column containing 5% Silicon OV-1 supported on 60–80 mesh Uniport KS, 80 °C, n-decane as an internal standard) showed it to contain 1a in 75% yield. Distillation (139–141 °C) of the reaction mixture and preparative GLC afforded the analytical sample. Analysis of the gas by GLC (a 2m × 3mm stainless steel tube containing Gasukuropack 54) showed it to contain ethylene.

For **1a**, IR(neat) 2944, 1250, 1172, 1010, 840, 755 cm^{-1}; NMR (CCl_4) δ 0.07(s, 18H), 6.53(s, 2H); mass spectrum *m/e* (relative intensity) 172(28), 157(53), 99(24), 73(100).

Anal. Found: P^+, 172.1103. $C_8H_{20}Si_2$ calcd.: P^+, 172.1104.

The chemical shifts of the olefinic proton of 1,1-bis(trimethylsilyl)ethene and (*E*)-1,2-bis(trimethylsilyl)ethene have been reported to be δ 6.25 and δ 6.56 in CCl_4 solution, respectively [13]. Furthermore, it is known that the IR spectrum of the (*E*) isomer of 1,2-bis(silyl)ethene shows a band at 1010 cm^{-1}, whereas the spectrum of the (*Z*) isomer has no absorption in this region [14].

1-(Triethylsilyl)-2-(trimethylsilyl)ethene (2). Bp 115–118 °C (15 Torr); IR(neat)

2940, 1460, 1420, 1250, 1175, 1010, 860, 840, 780, 720 cm^{-1}; NMR (CCl_4) δ 0.06 (s, 9H), 0.56(m, 6H), 0.93(m, 9H), 6.53(m, 2H); mass spectrum *m/e* (relative intensity) 214(13), 185(89), 157(42), 101(55), 87(100), 73(100). Anal. Found: C, 61.35; H, 12.31. $C_{11}H_{26}Si_2$ calcd.: C, 61.59; H, 12.22%.

*1,2-bis(dimethylethoxysilyl)ethene (**1b**).* Bp 74–77 °C (15 Torr); IR(neat) 2950, 1391, 1250, 1169, 1105, 1080, 1014, 950, 825, 784 cm^{-1}; NMR (CCl_4) δ 0.13(s, 12H), 1.13(t, *J* 7 Hz, 6H), 3.57(q, *J* 7 Hz, 4H), 6.53(s, 2H); mass spectrum *m/e* (relative intensity) 232(1), 217(80), 188(78), 163(34), 143(43), 133(89), 103(100), 75(38). Anal. Found: C, 51.46; H, 10.47. $C_{10}H_{24}O_2Si_2$ calcd.: C, 51.67; H, 10.41%.

*1,3-Bis(triethoxysilyl)ethene (**1c**).* Bp 135–140 °C (10 Torr); IR(neat) 2960, 1400, 1170, 1100, 1080, 1020, 960, 780 cm^{-1}; NMR (CCl_4) δ 1.20 (t, *J* 7 Hz, 18H), 3.77(q, *J* 7 Hz, 12H), 6.43(s, 2H); mass spectrum *m/e* (relative intensity) 308(78), 279(51), 252(45), 235(100), 223(35), 207(33), 163(44), 119(36). Anal. Found: C, 47.56; H, 9.20, $C_{14}H_{32}O_6Si_2$ calcd.: C, 47.69; H, 9.15%.

$Ru_3(CO)_{12}$-catalyzed reaction of styrene with trimethylsilylethene in the presence of a catalytic amount of triphenylsilane

A solution of styrene (10 mmol), trimethylsilylethene (20 mmol), $Ru_3(CO)_{12}$ (0.05 mmol), and triphenylsilane (0.5 mmol) in benzene (10 ml) was heated at 80 °C for 7 h with stirring. Analysis of the reaction mixture by GLC (130 °C, n-tetradecane as an internal standard) showed it to contain 1-trimethylsilyl-2-phenylethene (**4**) (59% yield based on styrene), **1a** (60% yield based on trimethylsilylethene), and styrene. The IR spectra, NMR spectra, and the retention time of **4** were consistent with those of an authentic sample prepared independently [6].

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