Ruthenium Complex-Catalyzed Silylation of Olefins. Selective Synthesis of Allylsilanes

Yoji HORI, Take-aki MITSUDO,* and Yoshihisa WATANABE*
Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606

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Synopsis. (1-2;5-6-η-Cyclooctadiene)(1-6-η-cyclooctatriene)ruthenium catalyzes the silylation of olefins at 60—140 °C to give allylsilanes with good selectivity in high yields. The reactions of trialkylsilane with 2-methyl-1-butene, 2-methyl-2-butene, and 3-methyl-1-butene give the same product, 3-methyl-1-trialkylsilyl-2-butene. Silylation of ethyl (*E*)-2-butenoate gives ethyl (*E*)-4-trialkylsilyl-2-butenoate in high yield.

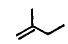
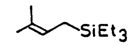
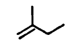
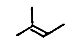
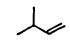
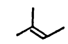
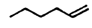
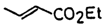
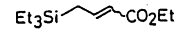
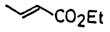
Allylsilanes are highly versatile synthetic intermediates.[1] Allylsilanes are prepared by 1) the reaction of allyl chloride with copper-silicon powder at 250 °C,[2-4] 2) Ni or Pd complex-catalyzed reactions of dienes with disilanes,[5-7] 3) hydrosilylation of dienes,[8-11] 4) dissolving metal reductions of aromatic hydrocarbons,[12] 5) Wittig reactions,[13-16] 6) silylation of allylic organometallics.[17,18] Recently, Seki et al. reported the preparation of vinylsilanes and allylsilanes from olefins and triethylsilane catalyzed by $[Ru_3(CO)_{12}]$.[19] In the course of our study on the organic syntheses catalyzed by (1-2;5-6-η-cyclooctadiene)(1-6-η-cyclooctatriene)ruthenium(0) [Ru(cod)(cot)] and its derivatives,[20] we found that Ru(cod)(cot) catalyzes the selective silylation of olefins which provides a versatile method of the preparation of allylsilanes.

Results and Discussion

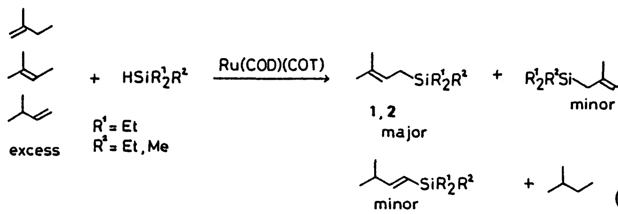
Triethylsilane and diethylmethylsilane readily reacted with 2-methyl-1-butene, 2-methyl-2-butene, 3-methyl-1-butene, 1-hexene, and ethyl (*E*)-2-butenoate in the presence of a catalytic amount of Ru(cod)(cot) at 60—140 °C to give the corresponding allylsilanes selectively. The results are summarized in Table 1.

The reactions of triethylsilane with 2-methyl-1-butene, 2-methyl-2-butene, or 3-methyl-1-butene gave 1-triethylsilyl-3-methyl-2-butene (**1**) as a major product in yields of 39—61% with 78—81% selectivity (Table 1, Runs 1—4). The minor products were regioisomers of **1**, (*E*)- and (*Z*)-1-trialkylsilyl-2-methyl-2-butene. Diethylmethylsilane also reacted with 2-methyl-2-butene to give 1-diethylmethylsilyl-3-methyl-2-butene (**2**) in a yield of 65% with 86% selectivity (Run 5). In all the reactions shown in Eq. 1, only small

Table 1. Selective Synthesis of Allylsilanes Catalyzed by Ru(cod) (cot)[a)]

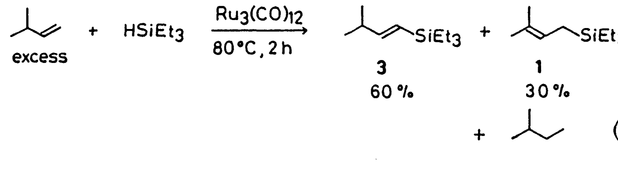
Run	Olefin	Silane	Temp °C	Time h	Total yield[b,c)] %	Product yield of **1**,**2**,**4**,**6**, or **7**/%[c)]
1		$HSiEt_3$	60	5	72	 **1** 56
2		$HSiEt_3$	80	2	76	**1** 59
3		$HSiEt_3$	80	2	75	**1** 61
4		$HSiEt_3$	80	2	49	**1** 39
5		$HSiEt_2Me$	80	2	(76)	 **2** 65
6		$HSiEt_3$	80	7	82	 **4** 67(*E*/*Z*=65/35)
7		$HSiEt_3$	140	0.5	(81)	**4** 66(*E*/*Z*=65/35)
8		$HSiEt_3$	80	2	(74)	 **6** 63(*E*/*Z*=91/9)
9		$HSiEt_2Me$	80	2	(74)	 **7** 66(*E*/*Z*=92/8)

a) Silane (10 mmol), olefin (50 mmol), catalyst (0.1 mmol). b) Total yield of silylated olefins. c) GLC yield (isolated yield based on the amount of hydrosilane).



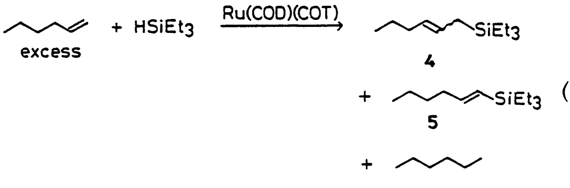
(1)

amounts of vinylsilanes were detected. Though Seki et al. reported that $[Ru_3(CO)_{12}]$ is an effective catalyst for the synthesis of vinylsilanes from olefins and hydrosilanes,[19] they did not mention the silylation of 2-methylbutenes. Several allylsilanes can be prepared by hydrosilylation catalyzed by Pd[8] and Rh[10] complexes. We confirmed that, in the presence of a catalytic amount of $[Ru_3(CO)_{12}]$, the reaction of triethylsilane with 3-methyl-1-butene gave (*E*)-1-triethylsilyl-3-methyl-1-butene (**3**) and **1** in yields of 60 and 30% respectively (Eq. 2). However, $[Ru_3(CO)_{12}]$ does not catalyze the reaction of triethylsilane with 2-methyl-1-butene and with 2-methyl-2-butene at 80 °C for 2 h; only the starting materials were recovered.



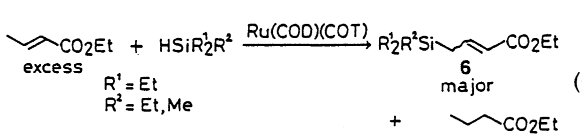
(2)

1-Hexene reacted with triethylsilane in the presence of Ru(cod)(cot) to give the product **4** in a yield of 67% (*E*/*Z*=65/35) with 82% selectivity (Run 6). (*E*)-1-Triethylsilyl-1-hexene (**5**) was also obtained in 15% yield. This result is almost the same as that of $[Ru_3(CO)_{12}]$-catalyzed reaction reported.[19] The reaction of triethylsilane with 1-hexene was rapid at 140 °C (Run 7). The yield and selectivity of products were the same as those in the reaction at 80 °C for 7 h (Runs 6, 7).



(3)

The reaction of ethyl (*E*)-2-butenoate with triethylsilane and with diethylmethylsilane gave the products **6** and **7** in yields of 63% (*E*/*Z*=91/9) and 66% (*E*/*Z*=92/8) with 85 and 89% selectivities (Runs 8, 9), respectively.

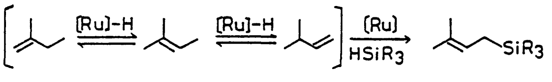


(4)

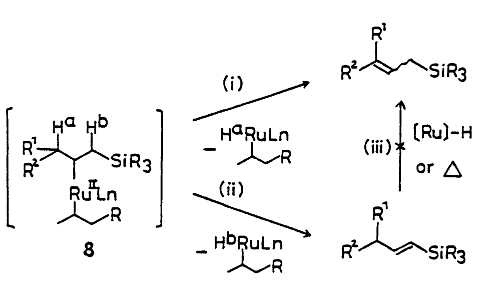
In these reactions, hydrogen did not evolve. In the reaction of ethyl (*E*)-2-butenoate, ethyl butanoate was formed in 92% yield based on triethylsilane.

When a catalytic amount of phosphorus ligands such as triphenylphosphine, tributylphosphine, triphenyl phosphite, and triethyl phosphite were added to the reaction mixture, no reaction occurred and starting materials, triethylsilane and olefins, were recovered. Dichlorotris(triphenylphosphine)ruthenium(II) $[RuCl_2(PPh_3)_3]$ was inactive in the reaction of triethylsilane with 2-methyl-2-butene. Silanes such as trimethoxysilane, triisopropylsilane, and dimethylphenylsilane, reacted with olefins. However, these reactions were very slow and only a trace amounts of the corresponding products were detected.

We consider the mechanism of the present reaction which is substantially the same as the $[Ru_3(CO)_{12}]$-catalyzed synthesis of vinylsilanes[19] except two features. The first one is a rapid equilibrium among three C_5 olefins, 2-methyl-1-butene, 2-methyl-2-butene, and 3-methyl-1-butene shown in Eq. 5. Probably a



(5)



8

(6)

catalytic amount of ruthenium hydride causes the isomerization of the double bond, then the silylation would occur. The second concerns a *β*-elimination step from an intermediate **8**[19] (Eq. 6). When two possible paths of *β*-elimination are considered in the last step of the present reaction, the path (i) would occur predominantly. The possibility of the isomerization of **3** to **1** was investigated. The reaction of a mixture of **3** and **1** (ratio **3**/**1**=68/32) in hexane was carried out in the presence of a catalytic amount of Ru(cot)(cod) and $HSiEt_3$ at 80 °C for 2 h; slight isomerization occurred (ratio **3**/**1**=54/46); however, the rate of the isomerization of vinylsilane to allylsilane (path (iii)) was very slow. Thus the product distribution would be determined by the direction of the *β*-elimination of **8**.

Experimental

All boiling points were uncorrected. Infrared spectra were recorded on a NICOLET 5-MX FT-IR spectrometer as films. Proton nuclear magnetic resonance spectra were obtained on a JNM-FX-90 spectrometer as 5—10% solutions with tetramethylsilane as an internal reference. Carbon-13 nuclear magnetic resonance spectra were obtained on a JNM-FX-100 (25.05 MHz) spectrometer as 40—50% solutions with tetramethylsilane and $CDCl_3$ as internal references. Mass spectra were taken on a Shimadzu QP-1000 GC-Mass spectrometer. Microanalyses were performed by the Laboratory for Organic Elemental Microanalysis of Kyoto University. Gas chromatographic analysis (GLC) were carried out on a 3 m×3 mm diameter column with OV 17 or a 2.9 m×3 mm diameter column with DEGA. All olefins, hydrosilanes, phosphines, and $[Ru_3(CO)_{12}]$ were commercial samples and were purified by distillation or by recrystallization under an atmosphere of argon before use. The complexes, Ru(cot)(cot)[21] and $[RuCl_2(PPh_3)_3]$[22] were prepared by the reported methods. All catalytic reactions were carried out under an atmosphere of argon.

General Reaction Procedure. The reaction of triethylsilane with ethyl (*E*)-2-butenoate is representative. A mixture of triethylsilane (1.16 g, 10 mmol), ethyl (*E*)-2-butenoate (5.71 g, 50 mmol), and Ru(cod)(cot) (0.032 g, 0.1 mmol) was heated in a 50 cm^3 autoclave at 80 °C for 2 h. Careful vacuum distillation of the reaction mixture afforded 1.69 g (yield 74%) of ethyl 4-triethylsilyl-2-butenoate (**5**). Other reactions were carried out in a similar manner. Allylsilanes (**4** and **5**) are known compounds.[19)]

1-Triethylsilyl-3-methyl-2-butene (1). Colorless liquid, bp 95 °C (22 mmHg) (1 mmHg=133.322 Pa); IR (neat) 1665 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=5.14 (1H, tqq, *J*=8.4 and 1.4 Hz), 1.68 (3H, s), 1.58 (3H, s), 1.41 (2H, d, *J*=8.4 Hz), 0.85—1.05 (9H, m), and 0.43—0.68 (6H, m); ^{13}C NMR (CDCl$_3$) δ=128.2 (s), 120.1 (d), 25.7 (q), 17.4 (q), 13.4 (t), 7.3 (q), and 3.3 (t). MS *m/z*: 184 (M$^+$). Found: C, 71.38; H, 13.37%. Calcd for $C_{11}H_{24}Si$: C, 71.65; H, 13.12%.

1-Diethylmethylsilyl-3-methyl-2-butene (2). Colorless liquid, bp 77 °C (22 mmHg); IR (neat) 1667 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=5.13 (1H, thep, *J*=8.5 and 1.3 Hz), 1.68 (3H, s), 1.56 (3H, s), 1.40 (2H, *J*=8.5 Hz, d), 0.84—1.04 (6H, m), 0.34—0.62 (4H, m), and −0.08 (3H, s); ^{13}C NMR(CDCl$_3$) δ=128.2 (s), 120.0 (d), 25.7 (q), 17.4 (q), 15.2 (t), 7.2 (q), 5.1 (t), and −6.3 (q). MS *m/z*: 170 (M$^+$). Found: C, 70.65; H, 13.31%. Calcd for $C_{10}H_{22}Si$: C, 70.50; H, 13.02%.

1-Triethylsilyl-3-methyl-1-butene (3). Colorless liquid, bp 80 °C (22 mmHg); IR (neat) 1615 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=6.03 (1H, dd, δ=18.9 and 5.8 Hz), 5.45 (1H, dd, *J*=18.9 and 1.1 Hz), 2.25 (1H, m), 0.99 (6H, d, *J*=6.8 Hz), 0.84—1.04 (9H, m), and 0.36—0.67 (6H, m); ^{13}C NMR(CDCl$_3$) δ=155.3 (d), 121.4 (d), 34.8 (d), 22.1 (q), 7.5 (q), and 3.9 (t). MS *m/z*: 184 (M$^+$). Found: C, 71.37; H, 13.38%. Calcd for $C_{11}H_{24}Si$: C, 71.65; H, 13.12%.

Ethyl (*E*)-4-Triethylsilyl-2-butenoate (6). Colorless liquid, bp 97 °C (2 mmHg); IR (neat) 1722 and 1644 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=7.07 (1H, td, *J*=9.0 and 15.4 Hz), 5.67 (1H, dt, *J*=15.4 and 1.3 Hz), 4.16 (2H, q, *J*=7.0 Hz), 1.76 (2H, dd, *J*=9.0 and 1.3 Hz), 1.28 (3H, t, *J*=7.0 Hz), 0.86—1.07 (9H, m), and 0.41—0.69 (6H, m); ^{13}C NMR (CDCl$_3$) δ=166.3 (s), 147.6 (d), 118.9 (d), 59.7 (t), 19.8 (t), 14.4 (q), 7.3 (q), and 3.3 (t). MS *m/z*: 228 (M$^+$). Found: C, 63.24; H, 10.76%. Calcd for $C_{12}H_{24}O_2Si$: C, 63.10; H, 10.59%.

Ethyl (*E*)-4-Diethylmethylsilyl-2-butenoate (7). Colorless liquid, bp 94 °C (3 mmHg); IR (neat) 1721 and 1644 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=6.96 (1H, dt, *J*=15.4 and 9.0 Hz), 5.57 (1H, dt, *J*=15.4 and 1.3 Hz), 4.06 (2H, q, *J*=7.2 Hz), 1.64 (2H, dd, *J*=9.0 and 1.3 Hz), 1.17 (3H, t, *J*=7.2 Hz), 0.70—0.96 (6H, m), 0.30—0.64 (4H, m), −0.10 (3H, s); ^{13}C NMR (CDCl$_3$) δ=165.4 (s), 146.6 (d), 118.5 (d), 58.8 (t), 20.5 (t), 13.6 (q), 6.4 (q), 4.2 (t), −7.1 (q). MS *m/z*: 214 (M$^+$). Found: C, 61.35; H, 10.64%. Calcd for $C_{11}H_{22}O_2Si$: C, 61.63; H, 10.34%.

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