APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 11, 667–671 (1997)

Ruthenium-Catalyzed Cross-Metathesis of Trisubstituted Vinylsilanes with Light Alkenes†

Zenon Foltynowicz[1] and Bogdan Marciniec[2]*

[1] Faculty of Commodity Science, Poznań University of Economics, al. Niepodległości 10, Pl-60 967 Poznań, Poland

[2] Faculty of Chemistry, A. Mickiewicz University, ul. Grunwaldzka 6, Pl-60 780 Poznań, Poland

In the cross-metathesis reaction of tri(methyl, ethoxy)vinylsilanes with propene and/or 1-butene catalyzed by $RuCl_2(PPh_3)_3$ activated in benzene at 115–130 °C, a series of l-alkenylsilanes of general formula $CH_3(CH_2)_mCH = CHSiMe_{3-n}(OEt)_n$, where $m = 0, 1$, and $n = 0–3$ (1-silyl-1-alkenes), as well as of formula $CH_2 = C(Me)SiMe_{3-n}(OEt)_n$, where $n = 1, 2$ (2-silyl-1-alkenes), were obtained. Additional products determined were allysilanes of general formula $CH_2 = CHCH_2SiMe_{3-n}(OEt)_n$ and $CH_3CH = CHCH_2SiMe_{3-n}(OEt)_n$, where $n = 1–3$. © 1997 by John Wiley & Sons, Ltd.

Appl. Organometal. Chem. **11**, 667–671 (1997)
No. of Figures: 4 No. of Tables: 0 No. of Refs: 12

Keywords: vinyl-substituted silanes; allylsilanes; short-chain alkenylsilanes; silylalkenes; ruthenium catalyst; cross-metathesis; dehydrogenative silylation; olefins; vinylsilane

Received 28 November 1995; accepted 7 May 1996

INTRODUCTION

The considerable utility of alkenylsilanes in a variety of chemical transformations as well as methods for their synthesis has been described elsewhere.[1–3] It has been possible to prepare an increasing number of 1-tri(methyl,alkoxysilyl)-1-alkenes via co-metathesis reaction of trisubstituted vinylsilanes with acyclic alkenes catalyzed by ruthenium catalysts. So far, this method has been very effective when liquid alkenes, i.e. from pentene to octadecene, have been applied.[2] As we previously reported, it was necessary to carry out the synthesis at a 15-fold excess of alkene in order to eliminate self-metathesis of vinylsilanes.[3] When propene was passed through the reactor containing a ruthenium catalyst and triethoxyvinylsilane, though propenylsilanes were obtained in 25% yield, the self-metathesis of vinylsilanes was the main reaction occurring, due to their excess in the reaction medium.[4] 1-Butenes do not give any products of co-metathesis under similar conditions.[4] Wakatsuki *et al.* reported on the preliminary attempt at the co-metathesis of trimethylvinylsilane with propene, but provided no data characterizing the products.[5] Therefore, the efficient co-metathesis of light alkenes, i.e. propene and 1-butene, with different vinylsilanes is described in this paper.

MATERIALS AND METHODS

Materials

Trimethylvinylsilane, ethoxydimethylvinylsilane, diethoxymethylvinylsilane and triethoxyvinylsilane were purchased from ABCR (Karlsruhe, Germany), and used without additional purification. Propene was from Merck (Darmstad, Germany) and 1-butene from Fluka AG (Buchs, Switzerland). Benzene and toluene were dried on molecular sieves. $RuCl_2(PPh_3)_3$ was prepared according to a standard procedure.

Measurements

GLC analyses were carried out on a Chromatron GChF 18.3 chromatograph. Co-metathesis products were analyzed on a 6 m steel column packed

---

* Correspondence to: Bogdan Marciniec.

† Part 14 in the series ‘Metathesis of Silicon-containing Olefins’; for Part 13, see [12].

Contract grant sponsor: National Committee of Scientific Research, Poland; Contract grant number: 7 S203 045 07.

with 10% SE-30 on Chromosorb P (programmed temp. rise 4 °C min^{-1}, helium carrier gas; thermal conductivity detector (TCD) detector). Alkenes were analyzed on a 3 m steel column packed with 23% SP-1700 on Chromosorb PAW (Supelco) (constant temp. 45 °C; carrier gas helium, FID detector).

NMR spectra were recorded on a Varian Gemini 300 MHz spectrometer. Mass spectra were obtained with a Finnigan MAT ITD 800 GC/MS spectrometer.

Synthetic procedures

General procedures of the co-metathesis reaction

Reactions were carried out in a stainless steel reactor (Roth GmbH, 50 ml capacity) with an inserted Teflon vial. The temperature was kept constant by a thermoregulated bath. Usually, 3 ml of vinylsilane was placed in a reactor and 1 ml of a benzene (or toluene in the case of reaction with propene) solution of 0.05 g $RuCl_2(PPh_3)_3$ (5.25×10^{-5} mol, described below as [Ru]) was added. After the reactor was tightly screwed up, an alkene was poured from a cylinder and compressed to 5.0 atm (propene) or 3.0 atm (1-butene). The reaction mixture was heated for 20 h at 115–130 °C. After that time alkenes were GLC-analyzed and the yield of the reaction was determined on the basis of vinylsilane.

Liquid products were purified from catalysts using column chromatography, isolated by vacuum distillation and identified spectroscopically. NMR data for allylsilanes,[8] bis(silyl)ethenes,[6, 7, 9] bis(silyl)propenes[10] and bis(silyl)butenes[6, 11] can be found in the respective literature.

Co-metathesis of trimethylvinylsilane with propene, I

The reaction of trimethylvinylsilane (3.0 ml, 2.07×10^{-2} mol) and propene (16 g, 0.4 mol) in the presence of the [Ru] catalyst at 130 °C yielded 45% of 1-(trimethylsilyl)-1-propene (*E*/*Z*=2:1), 40% of allyltrimethylsilane, 10% of bis(trimethylsilyl)ethene, and 5% of bis-(trimethylsilyl)propene. Their spectroscopic characteristics were in a good agreement with those already published.[6, 8, 10]

Co-metathesis of ethoxydimethylvinylsilane with propene, II

The reaction of ethoxydimethylvinylsilane (3.0 ml, 1.82×10^{-2} mol) and propene (16 g, 0.4 mol) in the presence of the [Ru] catalyst at 115 °C yielded 60% of **II**: 1-(ethoxydimethylsilyl)-1-propene (*E*/*Z*=5:1), 5% of 2-(ethoxydimethylsilyl)-1-propene, 20% of allylethoxydimethylsilane, 10% of bis(ethoxydimethylsilyl)ethene and 5% of bis(ethoxydimethylsilyl)propene.

^{13}C NMR (δ ppm):
II (*E*): 138.97 (=H*C*Si), 131.21 (*C*H=), 14.15 (–CH_3)

II (*Z*): 142.84 (=H*C*Si), 128.16 (*C*H=), 15.37 (–CH_3)

Co-metathesis of diethoxymethylvinylsilane with propene, III

The reaction of diethoxymethylvinylsilane (3.0 ml, 1.65×10^{-2} mol) and propene (16 g, 0.4 mol) in the presence of the [Ru] catalyst at 130 °C yielded 25% of **III**: 1-(diethoxymethylsilyl)-1-propene (*E*/*Z*=3:2), 5% of 2-(diethoxymethylsilyl)-1-propene, 20% of allyldiethoxymethylsilane, 30% of bis(diethoxymethylsilyl)ethene and 20% of bis(diethoxymethylsilyl)propene.

^{13}C NMR (δ ppm):
III (*E*): 125.33 (=H*C*Si), 146.45 (*C*H=), 22.45 (–CH_3)

III (*Z*): 123.91 (=H*C*Si), 146.94 (*C*H=), 21.86 (–CH_3)

Co-metathesis of triethoxyvinylsilane with propene, IV

The reaction of triethoxyvinylsilane (4.2 ml, 0.02 mol) and propene (16 g, 0.4 mol) in the presence of the [Ru] catalyst at 115 °C yielded 70% of **IV**: 1-(triethoxysilyl)-1-propene (*E*/*Z*=5:2), 15% of allyltriethoxysilane, 10% of bis(triethoxysilyl)ethene and 5% of bis(triethoxysilyl)propene. Their spectroscopic characteristics were satisfactorily consistent with those already published [9, 10].

Co-metathesis of trimethylvinylsilane with 1-butene, V

The reaction of trimethylvinylsilane (3.0 ml, 2.07×10^{-2} mol) and 1-butene (23 g, 0.4 mol) in the presence of the [Ru] catalyst at 130 °C yielded 20% of **Va**: 1-(trimethylsilyl)-1-butene (*E*/*Z*=3:1), 50% of **Vb**: 1-(trimethylsilyl)-2-butene (*E*/*Z*=7:5), 15% of bis(trimethylsilyl)ethene and 15% of bis(trimethylsilyl)butenes.

^{13}C NMR (*δ* ppm):
Va (*E*): 140.15 (=H*C*Si), 139.63 (*C*H=),
1.18 (–*C*H$_2$–), 12.91 (–*C*H$_3$)
Va (*Z*): 148.59 (=H*C*Si), 124.20 (*C*H=),
2.09 (–*C*H$_2$–), 18.53 (–*C*H$_3$)
Vb (*E*): 126.94 (=H*C*CH$_2$), 128.25 (*C*H$_3$*C*H=),
29.46 (–*C*H$_2$–), 15.50 (–*C*H$_3$)
Vb (*Z*): 122.99 (=H*C*CH$_2$), 130.79 (CH$_3$*C*H=),
22.68(–*C*H$_2$–), 15.50 (–*C*H$_3$)

Co-metathesis of ethoxydimethylvinylsilane with 1-butene, VI

The reaction of ethoxydimethylvinylsilane (3.0 ml, 1.82×10^{-2} mol) and 1-butene (23 g, 0.4 mol) in the presence of the [Ru] catalyst at 115 °C yielded 30% of **VIa**: 1-(ethoxydimethylsilyl)-1-butene (*E/Z*=2:1), 55% of **VIb**: 1-(ethoxydimethylsilyl)-2-butene (*E/Z*=7:4), 5% of bis(ethoxydimethylsilyl)ethene and 10% of bis(ethoxydimethylsilyl)butenes.

^{13}C NMR (*δ* ppm):
VIa (*E*): 138.93 (=H*C*Si), 131.41 (*C*H=),
1.07 (–*C*H$_2$–),
12.62 (–*C*H$_3$)
VIa (*Z*): 142.88 (=H*C*Si), 128.14 (*C*H=),
0.83 (–*C*H$_2$–),
15.34 (–*C*H$_3$)
VIb (*E*): 123.94 (=H*C*CH$_2$), 125.61 (CH$_3$*C*H=),
29.27 (–*C*H$_2$–), 15.34 (–*C*H$_3$)
VIb (*Z*): 121.94 (=H*C*CH$_2$), 129.07 (CH$_3$*C*H=),
22.36 (–*C*H$_2$–), 15.34 (–*C*H$_3$)

Co-metathesis of diethoxymethylvinylsilane with 1-butene, VII

The reaction of diethoxymethylvinylsilane (3.0 ml, 1.65×10^{-2} mol) and 1-butene (23 g, 0.4 mol) in the presence of the [Ru] catalyst at 130 °C yielded 20% of **VIIa**: 1-(diethoxymethylsilyl)-1-butene (*E/Z*=3:1), 40% of **VIIb**: 1-(diethoxymethylsilyl)-2-butene (*E/Z*=5:3), 20% of bis(diethoxymethylsilyl)ethene and 20% of bis(diethoxymethylsilyl)butenes.

^{13}C NMR (*δ* ppm):
VIIa (*E*): 135.03 (=H*C*Si), 146.97 (*C*H=),
1.08 (–*C*H$_2$–), 12.43 (–*C*H$_3$)
VIIa (*Z*): 133.53 (=H*C*Si), 148.05 (*C*H=),
3.05 (–*C*H$_2$–), 12.43 (–*C*H$_3$)
VIIb (*E*): 122.69 (=H*C*CH$_2$), 124.05 (CH$_3$*C*H=),
29.1 (–*C*H$_2$–), 15.1 (–*C*H$_3$)
VIIb (*Z*): 121.89 (=H*C*CH$_2$), 124.75 (CH$_3$*C*H=),
29.1 (–*C*H$_2$–), 15.1 (–*C*H$_3$)

Co-metathesis of triethoxyvinylsilane with 1-butene, VIII

The reaction of triethoxyvinylsilane (4.2 ml, 0.02 mol) and 1-butene (23 g, 0.4 mol) in the presence of the [Ru] catalyst at 115 °C proceeded with 45% conversion of vinylsilane and yielded 40% of **VIIIa**: 1-(triethoxysilyl)-1-butene (*E/Z*=7:1), 47% of **VIIIb**: 1-(triethoxysilyl)-2-butene (*E/Z*=6:1), 10% of bis(triethoxysilyl)ethene and 10% of bis(triethoxysilyl)butenes.

^{13}C NMR (*δ* ppm):
VIIIa (*E*): 117.39 (=H*C*Si), 154.94 (*C*H=),
1.01 (–*C*H$_2$–),
12.29 (–*C*H$_3$)
VIIIa (*Z*): 117.68 (=H*C*Si), 156.05 (*C*H=),
2.01 (–*C*H$_2$–), 13.82 (–*C*H$_3$)
VIIIb (*E*): 124.23 (=H*C*CH$_2$), 124.87
(CH$_3$*C*H=), 29.22
(–*C*H$_2$–), 11.78 (–*C*H$_3$)
VIIIb (*Z*): 122.89 (=H*C*CH$_2$), 123.43
(CH$_3$*C*H=), 27.90
(–*C*H$_2$–), 12.51 (–*C*H$_3$)

Co-metathesis of triethoxyvinylsilane with 1-butene, IX*

The reaction of triethoxyvinylsilane (2.1 ml, 0.01 mol) and 1-butene (23 g, 0.4 mol) in the presence of the [Ru] catalyst carried out at 115 °C for 10 h proceeded with 20% conversion of vinylsilane and gave 1-(triethoxysilyl)-1-butene (*E/Z*=8:1) in 90% yield and 10% of bis(triethoxysilyl)ethene.

Co-metathesis of triethoxyvinylsilane with 1-butene, X**

The reaction of triethoxyvinylsilane (2.1 ml, 0.01 mol) and 1-butene (23 g, 0.4 mol) in the presence of the [Ru] catalyst carried out at 115 °C for 20 h proceeded with 35% conversion of vinylsilane and yielded 80% of 1-(triethoxysilyl)-1-butene (*E/Z*=17:1), 5% of 1-(triethoxysilyl)-2-butene (*E/Z*=6:1) and 15% of bis(triethoxysilyl)ethene.

Co-metathesis of (*E*)-1,2-bis(triethoxysilyl)ethene with propene XI

The reaction (*E*)-1,2-bis(triethoxysilyl)ethene (1 ml, 2.5×10^{-3} mol) and 1-butene (23 g, 0.4 mol) were carried out in the presence of the [Ru] catalyst at 115 °C for 18 h. The conversion of bis(silyl)ethene was 30%.

$$\begin{gathered}
CH_2{=}CHCH_3 + CH_2{=}CHSiR_3 \\
{\scriptstyle -CH_2=CH_2}\downarrow{\scriptstyle [Ru]} \\
(Z)(E)\text{-}CH_3CH{=}CHSiR_3 + CH_2{=}CHCH_2SiR_3 + CH_2{=}C(CH_3)SiR_3 \\
+ (Z)(E)\text{-}R_3SiCH{=}CHSiR_3 + (Z)(E)\text{-}R_3SiCH{=}CHCH_2SiR_3
\end{gathered}$$

Scheme 1

RESULTS AND DISCUSSION

The co-metathesis of tri(methyl,alkoxy)vinylsilanes with light alkenes takes place in the presence of a benzene solution of $RuCl_2(PPh_3)_3$ mainly according to Scheme 1 for propene, and to Scheme 2 in the case of 1-butene.

Unlike in the open reactor conditions, both alkenes gave co-metathesis products under the conditions used (115–130 °C, 20 h). The reaction took place competitively with the isomerization of substrate and products as well as with the self-metathesis of vinylsilanes present in the reaction mixture. Vinylsilane self-metathesis, in the case of heavy alkenes, can be practically eliminated by the use of a 15-fold excess of alkenes,[1–4] which does not apply to the case of light alkenes. This may be explained by the volatility of propene and butene. In the latter case, even when the vinylsilane/alkene ratio equals 1:20, products of self-metathesis are still observed. The amount of side-reaction products can be limited at higher excesses of alkene. In the case of 1-butene quite good results were obtained under 40-fold excess of alkenes. Bis(triethoxysilyl)butene formation was practically eliminated. Shortening of the reaction time results in lower vinylsilane conversion, but isomerization of the main reaction product, i.e. 1-silyl-1-butene to 1-silyl-2-butene, was not observed.

The co-metathesis reaction involving gaseous alkenes did not occur below 100 °C. Two low-boiling vinylsilanes, i.e. trimethylvinylsilane and diethoxymethylvinylsilane, are not reactive at 115 °C either. More stringent conditions than for the other two vinylsilanes must be used, i.e. a higher temperature, 130 °C.

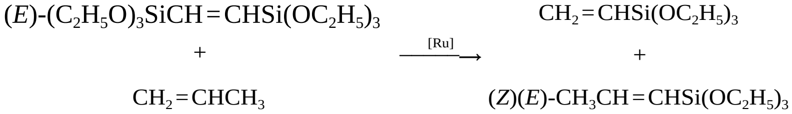
Specific short-chained alkenylsilanes were isolated as a mixture of isomers and were identified by NMR and GC–MS methods. Relevant data are given in the Experimental section. It should be mentioned that the formation of 1-propenylsilanes was accompanied by that of allylsilanes, as a result of their isomerization. The amount of allylsilane formed depends on the substituents on silicon. The highest yield was observed for trimethylvinylsilane, and the yield decreased with an increasing number of alkoxy substituents. The allylsilane and propenylsilanes are formed in comparable amounts when a trimethylvinylsilane and a diethoxymethylvinylsilane were applied, whereas ethoxydimethylvinylsilanes and triethoxyvinylsilanes gave predominantly propenylsilanes. Allylsilanes, i.e. 1-silyl-2-butenes, were also formed during co-metathesis of vinylsilanes with 1-butene, usually in a much higher yield than the expected 1-silyl-1-butenes. However, the terminal isomers, i.e. 1-silyl-3-butenes, were not observed.

Ethylene was detected as a gaseous product in both series of synthesis. Moreover, 1-butene was isomerized to 2-butenes. In practically every case the post-reaction mixture of butenes consisted of 1-butene, (*Z*) and (*E*) 2-butenes in a ratio of 1:1:5.

It was found that vinylsilane used in the formation of the self-metathesis product can be recycled. After isolation from the reaction mixture, (*E*)-1,2-bis(triethoxysilyl)ethene was subjected to the co-metathesis reaction with propene. Triethoxyvinylsilane and propenylsilanes were detected as the reaction products in a 1:1 ratio, indicating the occurrence of reversible co-metathesis of the self-metathesis product with

$$\begin{gathered}
CH_2{=}CHCH_2CH_3 + CH_2{=}CHSiR_3 \\
{\scriptstyle -CH_2=CH_2}\downarrow{\scriptstyle [Ru]} \\
(Z)(E)\text{-}CH_3CH_2CH{=}CHSiR_3 + (Z)(E)\text{-}CH_3CH{=}CHCH_2SiR_3 \\
+ (Z)(E)\text{-}R_3SiCH{=}CHSiR_3 + R_3SiCH_2CH{=}CHCH_2SiR_3
\end{gathered}$$

Scheme 2



$$\begin{array}{ccc} (E)\text{-}(C_2H_5O)_3SiCH{=}CHSi(OC_2H_5)_3 & & CH_2{=}CHSi(OC_2H_5)_3 \\ + & \xrightarrow{[Ru]} & + \\ CH_2{=}CHCH_3 & & (Z)(E)\text{-}CH_3CH{=}CHSi(OC_2H_5)_3 \end{array}$$

Scheme 3

$$R_3SiCH{=}CH_2 \xrightarrow[-CH_2=CH_2]{[Ru]} (E)\text{-}R_3SiCH{=}CHSiR_3 + (R_3Si)_2C{=}CH_2$$

Scheme 4

propene, according to Scheme 3.

Recent mechanistic investigations[5, 7] have shown that in the disproportionation of vinylsilanes, instead of C = C bond cleavage (formally characterizing the olefin metathesis), a new type of the olefin conversion occurs, namely the dehydrogenative silylation of olefins by vinylsilane.

The direct synthetic evidence for this new type of vinylsilane disproportionation is the formation of two organosilicon isomers, i.e. (*E*)-1,2-bis(silyl)ethene and 1,1-bis(silyl)ethene, according to Scheme 4.[7]

Our investigation of the co-metathesis with propene of vinylsilanes containing methyl substituents at silicon showed formation of 2-silyl-1-propene as a by-product beside (*E*) + (*Z*)-1-silyl-1-propenes. ^{13}C NMR spectra of the first product revealed signals that were attributed to the $=CH_2$ group [$\delta = 147.3$ ppm for $CH_2{=}C(Me)SiMe(OEt)_2$ and $\delta = 141.7$ ppm for $CH_2{=}C(Me)SiMe_2(OEt)$]. Presumably, because of a low concentration of the compounds in the reaction products, no signal has been observed which can be attributed to the quaternary carbon of these 2-silyl-1-propenes. No corresponding product in the co-metathesis of vinylsilanes with 1-butene has been detected so far.

We conclude that although the cross-metathesis is accompanied by numerous isomerization reactions, the ruthenium-catalyzed method can also be utilized for the synthesis of short-chained alkenylsilanes.

Acknowledgement This work was supported by funds from the National Committee of Scientific research (Project no. 7 S203 045 07).

REFERENCES

1. Z. Foltynowicz, *Polish J. Chem.* **67**, 1361 (1993).
2. Z. Foltynowicz and B. Marciniec, *J. Organomet. Chem.* **376**, 15 (1989).
3. Z. Foltynowicz, B. Marciniec and C. Pietraszuk, *J. Mol. Catal.* **65**, 113 (1991).
4. B. Marciniec, Z. Foltynowicz, C. Pietraszuk, J. Gulinski and H. Maciejewski, *J. Mol. Catal.* **90**, 213 (1994).
5. Y. Wakatsuki, H. Yamazaki, M. Nakano and Y. Yamamoto, *J. Chem. Soc., Chem. Commun.* 703 (1991).
6. B. Marciniec, C. Pietraszuk and Z. Foltynowicz, *J. Organomet. Chem.* **474**, 83 (1994).
7. B. Marciniec and C. Pietraszuk, *J. Chem. Soc., Chem. Commun.* 2003 (1995).
8. P. E. Rakita and L. S. Worsham, *J. Organomet. Chem.* **139**, 135 (1977).
9. B. Marciniec, H. Maciejewski, J. Gulinski and L. Rzejak, *J. Organomet. Chem.* **362**, 273 (1989).
10. B. Marciniec, Z. Foltynowicz and M. Lewandowski, *J. Mol. Catal.* **90**, 125 (1994).
11. L. D. Field, M. G. Gardiner, C. H. L. Kennard, B. A. Messerle and C. L. Raston, *Organometallics* **10**, 316 (1991).
12. E. S. Finkelshtein and B. Marciniec, in: *Progress in Organosilicon Chemistry,* Marciniec, B and Chojnowski, J. (eds), Gordon and Breach, Reading, 1995, p. 445.