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Metathesis of silicon-containing olefins: IX. Synthesis of 1-(trimethylsilyl)-1-alkenes by olefin metathesis[*]

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1-(Trimethylsilyl)-1-alkenes of general formula $CH_3(CH_2)_nCH{=}CHSi(CH_3)_3$, where $n=3$–15, have been prepared by a novel method, viz. by an effective cross-metathesis of vinyltrimethylsilane with 1-alkenes catalyzed by $RuCl_2(PPh_3)_3$. Excess of 1-alkene in the reaction mixture gave 1-(trimethylsilyl)-1-alkenes in good yields of up to 60% (in terms of vinylsilane). The products were identified by NMR spectroscopic (^1H, ^{13}C NMR) and GC MS methods.

Keywords: Silyl alkenes, preparation, ruthenium catalyst

INTRODUCTION

Alkenylsilanes exhibit considerable synthetic utility in organic synthesis,[1] mostly because of facile reaction with a range of electrophiles to give substitution products.[1,2] They have been widely applied as intermediates in stereoselective syntheses of alkenes,[2] pheromones[3] and other olefins.[4] Most known methods are based on silametallation,[5] hydrosilylation of alkynes[6] and conversion of alkynylsilanes, carbonyl compounds or vinyl halides.[2]

Recent advances in the metathetical activity of vinyl-trisubstituted silanes in the presence of ruthenium complexes allowed the introduction of a new, effective general method for synthesizing 1-silyl-1-alkenes based on the cross-metathesis of vinyl-trisubstituted silanes with 1-alkenes.[7–12] A synthetic method for silylalkenes involving trialkoxy-,[7,8] tri(methylalkoxy)-[9] and tri(phenylmethyl)-[9,10] substituents at silicon, was previously elaborated.

Our preliminary study on the cross-metathesis of vinyltrimethylsilane with 1-decene has shown an effective conversion when $RuCl_2(PPh_3)_3$ activated in benzene was used as catalyst.[9] Seki *et al.* showed high catalytic activity of $Ru_3(CO)_{12}$ promoted by silicon hydride in the cross-metathesis of vinyltrimethylsilane with styrene,[11] and Wakatsuki reported effective co-metathesis of vinyltrimethylsilane with 1-propene, styrene ($E:Z=99:1$) and methyl acrylate.[12] High metathetical activity of vinyltrimethylsilane in self-metathesis allows us to synthesize 1-(trimethylsilyl)-1-alkenes. This is a real advantage associated with use of the trimethylsilyl group in the vinylsilane since, after its desilylation, the by-product is hexamethyldisiloxane, which is volatile (b.p. 100 °C) and disappears on work-up.[2]

EXPERIMENTAL

Materials and measurements

Vinyltrimethylsilane was bought from Fluka AG (purum) and was used as received. Acyclic alkenes (purum, Fluka AG) were distilled prior to use. $RuCl_2(PPh_3)_3$ was obtained according to the standard procedure. ^1H and ^{13}C NMR spectra were measured on a Varian Gemini 300 MHz spectrometer in $CDCl_3$ or C_6D_6. Mass spectra were obtained on a Finnigan Mat JTD 800 GC MS spectrometer. Chromatographic GC analyses were performed on a Chromatron GCHF 18.3 gas chromatograph, equipped with a PC for data collection and treatment. Co-metathesis products were analyzed on a 3 m steel column packed with 10% SE 30 on Chromosorb P at programmed temperatures (100–280 °C min^{-1}). Helium was used as a carrier

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gas and a thermal conductivity detector (TCD) was the detector.

Co-metathesis reactions

General procedure

Reactions were carried out in Supelco glass vials sealed with a screw cap. All operations were done in air and no solvent was employed other than the excess of alkene. In a typical experiment 0.05 g (0.5 mmol) of $RuCl_2(PPh_3)_3$ dissolved in 1 cm^3 of dry benzene was added to a mixture of vinyltrimethylsilane (**I**) and alkene. The mixture was heated at 105 °C for 10 h, and products were analyzed by GC. After the catalyst had been removed by a column chromatography method, the product was isolated by vacuum distillation. Products were identified by GC MS and NMR techniques. Several 1-(trimethylsilyl)-1-alkenes of general formula $CH_3(CH_2)_nCH{=}CHSiMe_3$ (**II**) were prepared by the same method as described below.

1-(Trimethylsilyl)-1-hexene (IIa, *n* = 3)

To 0.05 g ruthenium catalyst in 1 cm^3 benzene, a mixture of 0.7 cm^3 (4.73 mmol) of vinyltrimethylsilane (**I**) and 2.96 cm^3 (25 mmol) of 1-hexene was added. The solution obtained was heated at 105 °C for 10 h. After the catalyst had been removed on a SiO_2 column, a product of the reaction was separated in 45% yield (based on vinylsilane), b.p. 55 °C/20 mm Hg.

MS: $m/z = 157(M^+)$, $141(M{-}CH_3)$, $83(M{-}SiMe_3)$, $73(SiMe_3)$.

^{1}H NMR (E isomer) ($CDCl_3$, δ, ppm): 6.03 (dt, $J = 18.5$, $CH{=}CSi$); 5.61 (dt, $J = 18.5$, $C{=}CHSi$).

1-(Trimethylsilyl)-1-heptene (IIb, *n* = 4)

To 0.05 g of ruthenium catalyst in 1 mol benzene, a mixture of the following reagents was added: 0.7 cm^3 (4.73 mmol) of **I** and 3.33 cm^3 (25 mmol) of 1-heptene. The mixture obtained was heated for 10 h at 105 °C. The reaction yield was 55% (based on **I**). Then the catalyst was separated and the product was distilled, b.p. 75 °C/20 mm Hg.

MS: $m/z = 171$ (M^+), 156 ($M{-}CH_3$), 98 ($M{-}SiMe_3$), 73 ($SiMe_3$).

^{1}H NMR (*E* isomer) ($CDCl_3$, δ, ppm): 6.05 (dt, $J = 18.5$, $CH{=}CSi$); 5.62 (dt, $J = 18.5$, $C{=}CHSi$).

^{13}C NMR (*E* isomer): 125.78 ($C{=}CSi$), 147.29 ($C{=}CSi$).

1-(Trimethyl)-1-octene (IIc, *n* = 5)

To 0.05 g of ruthenium catalyst in 1 cm^3 benzene, a mixture containing 0.7 cm^3 (4.73 mmol) of **I** and 3.77 cm^3 (25 mmol) of 1-octene was added. The solution obtained was heated in a tightly sealed vial for 10 h at 105 °C. The catalyst was removed on an SiO_2 column. The product of reaction was obtained in 50% yield (based on **I**), b.p. 85 °C/15 mm Hg.

MS: $m/z = 185$ (M^+), 169 ($M{-}CH_3$), 112 ($M{-}SiMe_3$), 73 ($SiMe_3$).

^{1}H NMR (*E* isomer) ($CDCl_3$, δ, ppm): 6.05 (dt, $J = 18.5$, $CH{=}CSi$); 5.63 (dt, $J = 18.5$, $C{=}CHSi$).

1-(Trimethylsilyl)-1-nonene (IId, *n* = 6)

To 0.05 g of ruthenium catalyst in 1 cm^3 benzene, a mixture of 0.7 cm^3 (4.73 mmol) of **I** and 4.1 cm^3 (25 mmol) of 1-nonene was added, followed by heating for 10 h at 105 °C. After the catalyst had been removed, the product was distilled off (b.p. 95–100 °C/15 mm Hg) with 45% yield.

MS: $m/z = 199$ (M^+), 183 ($M{-}CH_3$), 125 ($M{-}SiMe_3$), 73 ($SiMe_3$).

^{1}H NMR (*E* isomer) ($CDCl_3$, δ, ppm): 6.03 (dt, $J = 18.5$, $CH{=}CSi$); 5.61 (dt, $J = 18.5$, $C{=}CHSi$).

^{13}C NMR (*E* isomer) 129.32 ($C{=}CSi$), 147.28 ($C{=}CSi$).

1-(Trimethylsilyl)-1-decene (IIe, *n* = 7)

A portion of 0.05 g of $RuCl_2(PPh_3)_3$ was dissolved in 1 cm^3 of benzene and a mixture of 0.7 cm^3 (4.73 mmol) of **I** and 4.48 cm^3 (25 mmol) of 1-decene was added. The solution obtained was heated in a tightly sealed vial for 10 h at 105 °C. The reaction yield was 45% (based on **I**). After catalyst had been removed on an SiO_2 column from the reaction mixture, a product of co-metathesis was distilled, b.p. 120 °C/15 mm Hg.

MS: $m/z = 212$ (M^+), 197 ($M{-}CH_3$), 139 ($M{-}SiMe_3$), 73 ($SiMe_3$).

^{1}H NMR (*E* isomer) (C_6D_6, δ, ppm): 6.16 (dt, $J = 18.5$, $CH{=}CSi$); 5.80 (dt, $J = 18.5$, $C{=}CHSi$).

1-(Trimethylsilyl)-1-octadecene (IIf, *n* = 15)

To 0.075 g^3 of ruthenium catalyst in 1 cm^3 benzene, solutions containing 1.5 cm^3 of **I** (9.5 mmol) and 6 cm^3 (20 mmol) of octadecene were added. The reaction mixture obtained was heated for 10 h at 105 °C. Then the catalyst was separated on an SiO_2 column. After distillation (b.p. 185–190 °C/2 mm Hg), the product 1-(trimethylsilyl)-1-octadecene was obtained with a yield of 40%.

^{1}H NMR (*E* isomer) ($CDCl_3$, δ, ppm): 6.05 (dt, $J = 18.5$, $CH{=}CSi$); 5.60 (dt, $J = 18.5$, $C{=}CHSi$).

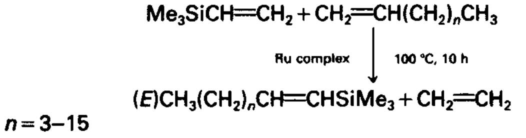
Table 1 Co-metathesis of 1-alkenes with vinyltrimethylsilane catalyzed by benzene solutions $RuCl_2(PPh_3)_3$[a]

Example	Alkene	$CH_2{=}CHSiMe_3$ conversion (%)	Yield of products (%)	
			(E)Silylalkene	Bis(silyl)ethene
IIa	1-Hexene	55	45	10
IIb	1-Heptene	60	55	5
IIc	1-Octene	55	50	5
IId	1-Nonene	45	45	0
IIe	1-Decene	50	45	2
IIf	1-Octadecene	40	40	0

[a] Reaction conditions: sealed Supelco vials, air, no solvent, 105 °C, 10 h.
IIa–e: $[\text{1-alkene}]:[CH_2{=}CHSiMe_3]:[Ru] = 1:5:0.1$
IIf: $[\text{1-alkene}]:[CH_2{=}CHSiMe_3]:[Ru] = 1:2:0.1$

RESULTS AND DISCUSSION

Cross-metathesis of vinyltrimethylsilane with 1-alkenes occurs in the presence of ruthenium catalyst at 100 °C, essentially according to Scheme 1.



$$\mathrm{Me_3SiCH{=}CH_2 + CH_2{=}CH(CH_2)_nCH_3} \xrightarrow[\text{100 °C, 10 h}]{\text{Ru complex}} (E)\mathrm{CH_3(CH_2)_nCH{=}CHSiMe_3 + CH_2{=}CH_2}$$

$n = 3$–15

Scheme 1

After longer reaction times, yields increase, but (E) is accompanied by products of alkene and silylalkene isomerizations. The results of catalytic experiments providing optimum conditions for the cross-metathesis in the synthesis of silylalkene are compiled in Table 1.

The reaction conversion, yield of silylalkene and bis(silyl)ethene were determined by GC analysis. Tris(triphenylphosphine) ruthenium dichloride complex dissolved in benzene in dry air appeared to be the most active catalyst in all the reactions studied. In contrast to vinyl[tri(methyl,-phenyl)]silanes, but similarly to vinylalkoxy-substituted silanes, vinyltrimethylsilane undergoes metathesis giving both stereo-isomers. In addition, some other by-products (especially for lighter homologous alkenes, $n = 3$–5) have also been formed which were identified by GC MS as regio-isomers of silylalkenes.

The distribution of all regio- and stereo-isomers changes with time of reaction since competitive isomerization of 1-alkenes to 2-alkenes, as well as of silyl-1-alkenes to silyl-2-alkenes, is observed similarly to co-metathesis of vinylalkoxy-substituted silanes with 1-alkenes.[13]

Further studies on the identification and determination of all the by-products will allow to optimization of synthesis of (E) isomers with a high yield.

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