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Metathesis of silicon-containing olefins

VIII. * Synthesis of alkenyl (phenyl, methyl) substituted silanes by olefin metathesis

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Abstract

1-Tri(phenyl, methyl)silyl-1-alkenes of the general formula $RCH{=}CHSiMe_{3-n}Ph_n$ (where $n = 1$–3, $R = C_mH_{2m+1}$, $m = 5$, 6, 8, 10, and 12; Ph) have been prepared by a novel method, *viz.* by a very effective cross-metathesis of vinyltri(phenyl, methyl)silanes with 1-alkenes and styrene catalyzed by ruthenium and rhodium complexes. A tenfold excess of 1-alkene in the reaction mixture gave stereospecific 1-tri(phenyl, methyl)silyl-1-alkenes (predominantly *E*-isomers) in high yields of up to 90% (in turn of vinylsilane). The products were identified by spectroscopic (IR, Raman, ^1H, ^{13}C NMR and GC-MS) methods.

1. Introduction

Alkenylsilanes have become reagents of great synthetic utility in organic chemistry [1]. Most of the known methods are based on silametallation [2] or hydrosilylation of alkynes [3] as well as on the transformation of alkynylsilanes, carbonyl compounds or vinyl halides [4].

Recent developments in the field of catalysis for metathesis of vinylsilanes and their cross-metathesis with olefins [5–7] have shown that this reaction is a novel, attractive, and universal method of synthesising a variety of alkenylsilanes and other silicon-containing olefins with an internal C=C bond.

Our study on the effect of the substituents at silicon in the cross-metathesis of vinyltrisubstituted silanes with 1-decene occurring in the presence of Ru-catalysts has also shown metathetical activity for vinylphenyl-substituted silanes [8]. Previously, we reported efficient self-metathesis of vinyltri(phenyl, methyl)silanes catalysed by various ruthenium as well as some rhodium complexes leading to synthesis of novel bis(silyl)ethenes according to eqn. (1) [9]:

$$\underset{n=1\text{–}3}{Ph_nMe_{3-n}SiCH{=}CH_2} \xrightarrow[-CH_2{=}CH_2]{} \underset{(Z+E)}{Ph_nMe_{3-n}SiCH{=}CHSiMe_{3-n}Ph_n} \quad (1)$$

The aim of this work is to present a synthetic method of obtaining various alkenyltri(phenyl, methyl)silanes including styrylsilanes, based predominantly on cross-metathesis of vinylsilanes $CH_2{=}CHSiPh_2Me$ and $CH_2{=}CHSiPhMe_2$ with alkenes and styrene.

2. Results and discussion

The cross-metathesis of vinyldimethylphenylsilane, vinylmethyldiphenylsilane and vinyltriphenylsilane with 1-alkenes and styrene occurs in the presence of ruthenium and rhodium catalysts at 80–130°C, mainly according to the following general scheme (eqn. (2)):

$$CH_2{=}CHSiMe_{3-n}Ph_n + CH_2{=}CHR \xrightarrow{Ru,Rh\ cat.} E - RCH{=}CHSiMe_{3-n}Ph_n + CH_2{=}CH_2 \quad (2)$$

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TABLE 1. Catalytic cross-metathesis of vinyltri(phenyl, methyl)silanes with 1-alkenes and styrene

1-Alkene	Catalyst	Conditions temperature/time (°C/h)	Products yield (%) (E/Z)
CH_2=$CHSiMe_2Ph$			
1-Heptene	$RuCl_2(PPh_3)_3/C_6H_6$	Reflux/48	60 (45/1)
	$RuCl_2(PPh_3)_3/C_6H_6$	130/48	70
	$RuCl_2(PPh_3)_3$	130/48	60
1-Octene	$RuCl_2(PPh_3)_3/C_6H_6$	Reflux/4	70 (20/1)
	$RuCl_2(PPh_3)_3$	130/48	80
1-Decene	$RuCl_2(PPh_3)_3/C_6H_6$	130/2	70 (50/1)
	$RuCl_2(PPh_3)_3$	130/48	85
	$[RuCl_2(CO)_3]_2$	130/48	85
	$Ru_2(acac)_3$	130/48	50
	$RhCl(PPh_3)_3$	130/48	40
1-Dodecene	$RuCl_2(PPh_3)_3/C_6H_6$	130/4	65 (16/1)
	$RuCl_2(PPh_3)_3$	130/48	80
1-Tetradecene	$RuCl_2(PPh_3)_3/C_6H_6$	130/6	65 (20/1)
	$RuCl_2(PPh_3)_3$	130/48	70
1-Octadecene	$RuCl_2(PPh_3)_3/C_6H_6$	130/6	70
	$RuCl_2(PPh_3)_3$	130/48	75
Styrene	$[RuCl_2(CO)_3]_2$	120/0.3	85 (40/1)
	$RuCl_2(PPh_3)_3/C_6H_6$	120/0.3	85
CH_2=$CHSiMePh_2$			
1-Decene	$RuCl_2(PPh_3)_3/C_6H_6$	130/6	70 (50/1)
CH_2=$CHSiPh_3$			
1-Decene	$RuCl_2(PPh_3)_3/C_6H_6)$	150/24	30

($n = 1$, $R = C_5H_{11}$, C_6H_{13}, C_8H_{17}, $C_{10}H_{21}$, $C_{12}H_{25}$, $C_{16}H_{33}$ or Ph; $n = 2$, $R = C_8H_{17}$; $n = 3$, $R = C_8H_{17}$). Contrary to trialkoxy- and tri(methyl, alkoxy)-substituted silanes, vinylphenyl-substituted silanes undergo cross-metathesis with very high stereoselectivity (more than 90% of E-products). In addition, some other by-products (especially for higher homologous of alkenes) have also been formed, which were identified as isomers of alkenylsilanes.

The ruthenium and rhodium complexes, $RuCl_2(PPh_3)_3/C_6H_6$, $RuCl_2(PPh_3)_3$, $[RuCl_2(CO)_3]_2$, $Ru(acac)_3$ and $RhCl(PPh_3)_3$, were used to catalyze these reactions.

The results of catalytic experiments leading to the optimum catalyst activity and conditions of the reactions in the synthesis of alkenylsilanes (and styrylsilane) are compiled in Table 1. The reaction yield and E/Z ratio were calculated on the basis of the GLC analysis. Ruthenium dichloride tris(triphenylphosphine)complex dissolved preliminarily in benzene appeared to be the most active in all the reactions examined.

The co-metathesis of vinylsilane with styrene occurs very quickly and efficiently, giving stereospecific E-styrylsilane. The same compound was reported to be the product of dehydrogenative silylation of styrene proceeding at 50–160°C (in benzene or without solvents in nitrogen) according to eqn. (3) [10]:

$$PhCH{=}CH_2 + HSiR^1_2R^2 \xrightarrow{Ru_3(CO)_{12}} E\text{-}PhCH{=}CHSiR^1_2R^2 + PhCH_2CH_3 \quad (3)$$

($R^1R^2 = Et$; $R^1 = Me$, $R^2 = Ph$)

i.e. under conditions close to those for co-metathesis. However, the metathetical route seems to be more attractive since the styrylsilane is the only product dissolved in the reaction mixture (besides the CH_2=CH_2 evolved). No product of styrene polymerization was detected.

Specific alkenylsilanes and styrylsilane were isolated and identified by spectroscopic (IR, ^1H, ^{13}C NMR, Raman and GC-MS) methods. The *trans*-configuration of the C–H bond at the C=C bond was identified by the presence of a medium band at 990 cm^{-1} in the IR spectrum corresponding to the band of the C–H bond which is not seen in the Raman spectra. The ^1H and ^{13}C NMR spectra of six alkenylsilanes and styrylsilane were recorded and assigned by comparison with those reported in the literature [10–19].

The complementary GC-MS method gave very useful information. Chromatographic distribution of all the products followed by their mass-spectroscopic identification allowed most of the by-products to be evaluated as regio- and stereo-isomers.

All the details on the synthesis procedures and spectroscopic identification of the products are presented in the Experimental section.

3. Experimental details

3.1. Materials

The 1-alkenes and styrene were purchased from Fluka. Vinyldimethylphenylsilane and vinyltriphenylsilane were obtained from ABCR. Vinylmethyldiphenylsilane was prepared using vinylmethyldichlorosilane and phenyllithium. $Ru(acac)_3$ was purchased from Strem Chemicals; $RuCl_2(PPh_3)_3$, $[RuCl_2(CO)_3]_2$ and $RhCl(PPh_3)_3$ were prepared by standard procedures.

3.2. Equipment and analytical measurements

Infrared spectra were recorded on a Perkin–Elmer Model 180 spectrophotometer and Raman spectra on a Raman Spectrometer Bomem MB 152. ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 300 spectrometer. All chemical shifts are referenced to TMS. Gas chromatography was carried out with a HP 5890 instrument using a 1.8 m steel column packed with 10% SE-30 on Chromosorb WHP (with TCD). GC-MS analysis were performed on a Varian 3300 Gas chromatograph (30 m fused silica capillary column

DB-1) connected with a Finnigan MAT ITD 800 mass spectrometer.

3.3. Synthetic procedures

3.3.1. General procedure of the cross-metathesis reaction

The vinylsilane (5.5 mmol) and 1-alkene or styrene (55 mmol) were placed in glass ampoules (or in a flask equipped with a condenser) and then 0.055 mmol of the catalyst ($RuCl_2(PPh_3)_3$ dissolved in 11 mmol of degassed benzene, $RuCl_2(PPh_3)_3$, $[RuCl_2(CO)_3]_2$, Ru-$(acac)_3$, $RhCl(PPh_3)_3$) was added. Sealed ampoules (or flasks) were heated at 110–130°C for several hours. The yield of the reaction products and the ratio of E/Z isomers were calculated by the GLC method. Liquid products were isolated and purified using column chromatography (Silicagel MN-60) and distillation under a vacuum. All reactions were carried out in dry air and in the absence of solvent.

3.3.2. 1-Dimethylphenylsilyl-1-heptene (Ia)

The reaction mixture of the catalyst (0.0527 g of $RuCl_2(PPh_3)_3$ dissolved in 1 cm^3 of degassed benzene), vinyldimethylphenylsilane (1 cm^3) and 1-heptene (7.8 cm^3) was heated for 48 h under reflux and yielded 60% of alkenylsilane, $E/Z = 45/1$.

IR (film): ν(C=C) = 1615, ν(HC=CH(*trans*)) = 990 cm^{-1}. ^{1}H NMR ($CDCl_3$, TMS): δ 0.31 (s, 6H); 6.15 (dt, $J = 18.5$, C=CHSi); 5.76 (dt, $J = 18.5$, HC=CSi); 7.29–7.57 (m, 5H); 0.88 (t, 3H); 1.2–1.43 (m, 6H); 1.6–2.1 (m, 2H) ppm. ^{13}C NMR: −2.44 ($SiCH_3$); 127.38 (C=*C*Si); 149.59 (*C*=CSi); 127.81, 128.89, 133.94 (Ph). MS (rel. intensity); m/z 232 (M, 8); 217(77); 155(27); 135(100).

3.3.3. 1-Dimethylphenylsilyl-1-octene (Ib)

The reaction mixture of the catalyst (0.0527 g of $RuCl_2(PPh_3)_3$ dissolved in 1 cm^3 of degassed benzene), vinyldimethylphenylsilane (1 cm^3) and 1-octene (8.6 cm^3) was heated for 4 h under reflux and yielded 70% of alkenylsilane, $E/Z = 20/1$.

IR (film); ν(C=C) = 1618, ν(HC=CH(*trans*)) = 990 cm^{-1}, ^{1}H NMR ($CDCl_3$, TMS): δ 0.31 (s, 6H); 6.14 (dt, $J = 18.5$, C=CHSi); 5.72 (dt, $J = 18.5$, HC=CSi); 7.26–7.57 (m, 5H); 0.88 (t, 3H); 1.2–1.5 (m, 8H); 1.6–2.1 (m, 2H) ppm. ^{13}C NMR: −2.38 ($SiCH_3$); 127.22 (C=*C*Si); 149.43 (*C*=CSi); 127.65, 128.73, 133.83 (Ph). MS (rel. intensity); m/z 246 (M, 15); 231(100); 169(94); 135(31); (see [11]).

3.3.4. 1-Dimethylphenylsilyl-1-decene (Ic)

The reaction mixture of the catalyst (0.0527 g of $RuCl_2(PPh_3)_3$ dissolved in 1 cm^3 of degassed benzene), vinyldimethylphenylsilane (1 cm^3) and 1-decene (10.4 cm^3) was heated for 4 h at 130°C and yielded 70% of alkenylsilane, $E/Z = 50/1$.

IR (film): ν(C=C) = 1618, ν(HC=CH(*trans*)) = 990 cm^{-1}. ^{1}H NMR ($CDCl_3$, TMS): δ 0.31 (s, 6H); 6.14 (dt, $J = 18.5$, C=CHSi); 5.72 (dt, $J = 18.5$, HC=CSi); 7.27–7.52 (m, 5H); 0.88 (t, 3H); 1.2–1.53 (m, 12H); 1.6–2.0 (m, 2H) ppm. ^{13}C NMR: −2.27 ($SiCH_3$); 127.09 (C=*C*Si); 149.37 (*C*=CSi); 127.59, 128.68, 133.73 (Ph). MS (rel. intensity): m/z 274 (M, 14); 259(28), 197(77), 135(100) (see [17]).

3.3.5. 1-Dimethylphenylsilyl-1-dodecene (Id)

The reaction mixture of the catalyst (0.0527 g of $RuCl_2(PPh_3)_3$ dissolved in 1 cm^3 of degassed benzene), vinyldimethylphenylsilane (1 cm^3) and 1-dodecene (12.2 cm^3) was heated for 4 h under reflux, yielding 70% of alkenylsilane $E/Z = 16/1$.

IR (film): ν(C=C) = 1615, ν(HC=CH(*trans*)) = 990 cm^{-1}. ^{1}H NMR ($CDCl_3$, TMS): δ 0.31 (s, 6H); 6.14 (dt, $J = 18.5$, C=CHSi); 5.72 (dt, $J = 18.5$, HC=CSi); 7.29–7.59 (m, 5H); 0.88 (t, 3H); 1.2–1.5 (m, 16H); 1.9–2.2 (m, 2H) ppm. ^{13}C NMR; −2.38 ($SiCH_3$); 127.27 (C=*C*Si); 149.48 (*C*=CSi); 127.70, 128.79, 133.83 (Ph). MS (rel. intensity): m/z 302 (M, 25); 287 (67); 225 (100); 135 (20), (see [12,13]).

3.3.6. 1-Dimethylphenylsilyl-1-tetradecene (Ie)

The reaction mixture of the catalyst (0.0527 g of $RuCl_2(PPh_3)_3$ dissolved in 1 cm^3 of degassed benzene), vinyldimethylphenylsilane (1 cm^3) and 1-tetradecene (13.9 cm^3) was heated for 6 h at 130°C, yielding 65% of alkenylsilane, $E/Z = 20/1$.

IR (film): ν(C=C) = 1615, ν(HC=CH(*trans*)) = 990 cm^{-1}. ^{1}H NMR ($CDCl_3$, TMS): δ 0.31 (s, 6H); 6.14 (dt, $J = 18.5$, C=CHSi); 5.72 (dt, $J = 18.5$, HC=CSi); 7.25–7.57 (m, 5H); 0.88 (t, 3H); 1.2–1.6 (m, 20H); 2.0–2.2 (m, 2H) ppm. ^{13}C NMR: −2.26 ($SiCH_3$); 127.08 (C=*C*Si); 149.37 (*C*=CSi); 127.58, 128.79, 133.83 (Ph), MS (rel. intensity): m/z 330 (M, 27); 315 (59); 253 (75); 135 (100).

3.3.7. 1-Dimethylphenylsilylstyrene (If)

The reaction mixture of the catalyst (0.0527 g of $RuCl_2(PPh_3)_3$ dissolved in 1 cm^3 of degassed benzene), vinyldimethylphenylsilane (1 cm^3) and styrene (6.3 cm^3) was heated for 0.3 h at 120°C, yielding 85% of styrylsilane, $E/Z = 40/1$.

IR (film): ν(C=C) = 1605, ν(HC=CH(*trans*)) = 990 cm^{-1}. ^{1}H NMR ($CDCl_3$, TMS): δ 0.42 (s, 6H); 6.55 (d, $J = 19.2$, C=CHSi); 6.97 (d, $J = 19.2$, HC=CSi); 7.01–7.61 (m, 10H) ppm. ^{13}C NMR: −2.34 ($SiCH_3$); 127.01 (C=*C*Si); 145.19 (*C*=CSi); 126.42, 127.73, 128.06, 128.43, 128.96, 133.82 (Ph). MS (rel. intensity): m/z 238 (M, 32); 223 (100); 161(24); 135(10) (see [10,14–18]).

*3.3.8. 1-Methyldiphenylsilyl-1-decene (**II**)*

The reaction mixture of the catalyst (0.0427 g of $RuCl_2(PPh_3)_3$ dissolved in 1 cm^3 of degassed benzene), vinylmethyldiphenylsilane (1 cm^3) and 1-decene (12.5 cm^3) was heated for 6 h at 130°C, yielding 60% of alkenylsilane, $E/Z = 40/1$.

IR (film): ν(C=C) = 1615, ν(HC=CH(*trans*)) = 990 cm^{-1}. ^1H NMR ($CDCl_3$, TMS); δ 0.59 (s, 3H); 6.20 (dt, $J = 18.5$, C=CHSi); 5.90 (dt, $J = 18.5$, HC=CSi); 7.28–7.64 (m, 10H); 0.88 (t, 3H), 1.2–1.6 (m, 12H); 1.9–2.2 (m, 2H) ppm. ^{13}C NMR: −3.48 ($SiCH_3$); 127.76 (C=*C*Si); 151.55 (*C*=CSi); 127.65, 128.99, 134.72 (Ph). MS (rel. intensity): m/z 336 (M, 12); 321(37); 259(100); 199(15).

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