

Hydrosilylation of ethynylsilanes with dimethyl(2-thienyl)silane

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Abstract

The hydrosilylation of ethynylsilanes $RC\equiv CH$ ($R = Me_3Si, Cl_3Si, (EtO)_3Si, N(CH_2CH_2O)_3Si$) in the presence of Speier's catalyst gives predominantly the β -*trans*-isomer, which in the case of ethynylsilatrane is the only product formed. The reaction of trimethylethynylsilane and its carbon analogue, *t*-butylacetylene, with dimethyl(2-thienyl)silane in the presence of rhodium catalysts occurs less selectively to afford both the hydrosilylation products and the products of dehydrocondensation. In some cases, a product of double bond hydrogenation is also formed.

Introduction




Recently we have reported the hydrosilylation of the triple bond $C\equiv C$ in *N*-propargylamines, propargyl alcohol, methylpropargyl ether, 2-propargylthiophene, 2-ethynylthiophene, phenylacetylene, methyl propiolate [1] and 1-ethynyladamantane [2] with phenyl- and thienyl-hydrosilanes. In order to examine how the direction of the hydrosilylation of ethynylsilanes depends on the electronic effects of different silyl groups in ethynylsilanes, the addition of dimethyl(2-thienyl)silane to trimethyl-, triethoxy-, and trichloro-(ethynyl)silanes and ethynylsilatrane was carried out.

Results and discussion

According to literature data [3], the hydrosilylation of trichloro(ethynyl)silane [3] with trichloro-, dimethylchloro-, and trimethyl-silanes in the presence of Speier's catalyst yields two products (the β -*trans*- and the α -isomer), the amount of α -isomer in the hydrosilanes studied increasing from 16 to 75%. The hydrosilylation of alkylalkoxyethynylsilanes $R_n(R'O)_{3-n}SiC\equiv CH$ with chloroalkylsilanes [4,5] gives only the β -*trans*-isomer in the presence of $H_2PtCl_6 \cdot 6H_2O$.

Trimethyl-, triethoxy- and trichloro-(ethynyl)silanes react with dimethyl(2-thienyl)silane in the presence of chloroplatinic acid to afford the β -*trans*- and

Table 1
Hydroxylation of ethynylsilatrane with arylsilanes Ar_nSiMe_{3-n}H (50 °C, 6 h, catalyst H₂PtCl₆·6H₂O)

Ar	n	Yield (%)	m.p. (°C)	δ(¹ H) (ppm)				O-CH ₂	HC=CH ^a	Ar	Mass spectral data <i>m/z</i> (intensity, % of the maximum)
				Si-CH ₃	N-CH ₂	N-CH ₂	O-CH ₂				
	1	58	146	0.35(s,6)	2.82(t,6)	2.82(t,6)	3.78(t,6)	6.51(d,1) 6.80(d,1)	7.19-7.60(3)	341(M ⁺ , 0.5), 326(10), 175(13), 174(100)	
	2	35	123	0.49(s,3)	2.82(t,6)	2.82(t,6)	3.80(t,6)	6.62(d,1) 6.89(d,1)	7.20-7.62(6)	409(M ⁺ , 0.8), 175(13), 174(100), 57(11), 55(12), 45(14), 43(19), 41(15), 28(25)	
	3	45	166	-	2.80(t,6)	2.80(t,6)	3.80(t,6)	6.69(d,1) 6.98(d,1)	7.21-7.63(9)		
Ph	1	62	126	0.29(s,6)	2.79(t,6)	2.79(t,6)	3.78(t,6)	6.48(d,1) 6.79(d,1)	7.31-7.58(5)	335(M ⁺ , 0.3), 175(13), 174(100), 28(23)	
Ph	2	39	132	0.37(s,3)	2.80(s,3)	2.80(s,3)	3.85(t,6)	6.57(d,1) 6.87(d,1)	7.32-7.50(10)		
Ph	3	47	210	-	2.86(t,6)	2.86(t,6)	3.80(t,6)	6.66(d,1) 6.92(d,1)	7.31-7.54(15)		

^a *J* of vinyl protons vary within the 18.8-19.2 Hz range.

Table 2

Hydroosilylation of ethynylsilanes and *t*-butylacetylene $\text{RC}\equiv\text{CH}$ with dimethyl(2-thienyl)silane (50°C , 6 h, catalyst $\text{H}_2\text{PtCl}_6\cdot 6\text{H}_2\text{O}$) and ^1H NMR data for the mixture of isomers

R	Yield (%) (GC data)	β - <i>trans</i> -/ α -isomer ratio (GC and ^1H NMR data)	$\delta(^1\text{H})$ NMR (ppm)				
			R	SiMe	HC=CH	=CH ₂	thiophene ring protons
Me ₃ Si	99	76/24	0.07; 0.09	0.60; 0.65	7.15 (¹ J 22 Hz) 7.31 (¹ J 22 Hz)	6.91 (¹ J 1 Hz)	7.21–7.60
Cl ₃ Si	79	66/34	-	0.59; 0.65	6.31 (¹ J 21 Hz) 7.00 (¹ J 21 Hz)	6.33 (¹ J 3 Hz) 6.64 (¹ J 3 Hz)	7.24–7.60
(EtO) ₃ Si	82	75/25	1.22 (CH ₃) 3.80 (CH ₂ O)	0.59; 0.67	6.02 (¹ J 22 Hz) 6.84 (¹ J 22 Hz)	6.03 (¹ J 4 Hz) 6.22 (¹ J 4 Hz)	7.20–7.56
$\overline{\text{N}(\text{CH}_2\text{CH}_2\text{O})_3\text{Si}}$	58 ^a	100/0	2.82 (CH ₂ N) 3.78 (CH ₂ O)	0.61	6.51 (¹ J 19 Hz) 6.80 (¹ J 19 Hz)	-	7.19–7.60
<i>t</i> -Bu	78	96/4	1.29	0.64	5.93 (¹ J 19 Hz) 6.44 (¹ J 19 Hz)	-	7.26–7.54

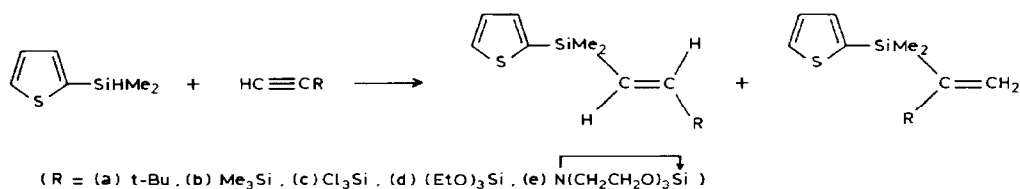
^a Preparative yield.

Table 3

 ^{13}C NMR data for the ethynyl group of silanes $\text{RC}\equiv\text{CH}$

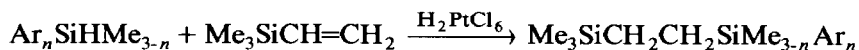
R	$\delta(^{13}\text{C})$ (ppm)	
	C_α	C_β
Me_3Si	89.28	93.71
Cl_3Si	81.31	93.71
$(\text{EtO})_3\text{Si}$	81.76	92.87
$\text{N}(\text{CH}_2\text{CH}_2\text{O})_3\text{Si}$	91.85	84.43
t-Bu	89.70	62.96

α -isomers. The reaction of ethynylsilatrane with phenyl- and thienyl-silanes $\text{Ar}_n\text{SiHMe}_{3-n}$ occurs stereo- and regio-selectively to yield solely the β -*trans* product (see Table 1).



Trimethylethynylsilane reacts with dimethyl(2-thienyl)silane at 50°C for 6 h almost quantitatively to give the β -*trans*- and α -isomers in a 76/24 ratio, whereas t-butylacetylene, the carbon analogue of trimethylethynylsilane, is less reactive (yield 78%) and acts more regioselectively (β -*trans*-/ α - 96/4) [2]. The substitution of methyl groups at the silicon atom by the electron acceptor chloro or ethoxy groups decreases, to some extent, the reaction yield without affecting significantly the product ratio (Table 2). This is in good agreement with the ^{13}C NMR data (Table 3). The higher electron density on the β -carbon atom of the ethynyl group in ethynylsilatrane and t-butylacetylene compares with the α -carbon atom leads to a β -adduct (Table 2).

In contrast to trimethylethynylsilane, the hydrosilylation of trimethylvinylsilane with thienyl- and phenyl-silanes in the presence of Speier's catalyst affords only the β -isomer (Table 4).



(Ar = 2-thienyl, phenyl; $n = 1-3$)

The reaction proceeds readily in 86–99% yield at 50°C .

Besides chloroplatinic acid, rhodium complexes were also employed to investigate how the catalyst affects the regioselectivity and stereospecificity of the hydrosilylation of ethynylsilanes and t-butylacetylene with dimethyl(2-thienyl)silane. According to ref. 6–8, hydrosilylation of phenylacetylene and 1-hexyne with triethyl-, ethyldichloro- and trichloro-silane on $\text{RhCl}_3 \cdot 4\text{H}_2\text{O}$, $[(\text{RhCOCl})_2\text{C}_4\text{H}_6]_n$, and $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ catalysts is non-stereospecific and leads to a mixture of *cis*- and *trans*-addition products. The regioselectivity depends on the structure of the acetylene compound: the addition of alkyl- and chloro-hydrosilanes to 1-hexyne [7] results in a mixture of β -products and in a mixture of α - and β -isomers in the case

Table 5

Hydrosilylation of trimethylethynylsilane and t-butylacetylene ($\text{Me}_3\text{MC}\equiv\text{CH}$) with dimethyl(2-thienyl)silane on rhodium catalysts (6 h)

M	Catalyst	T ($^{\circ}\text{C}$)	Yield (%) (GC data)	Product ratio I/II/III/IV (GC data)
Si	$\text{RhCl}(\text{PPh}_3)_3$	50	93	63/21/16/0
Si	$\text{RhCl}_3 \cdot 4\text{H}_2\text{O}$	50	91	74/17/8/1
Si	$[(\text{P})\text{-CH}_2\text{P}^+\text{Bu}_3][\text{RhCl}_4]^-$	50	64	71/17/9/3
Si	$[\text{Et}_3\text{N}^+\text{CH}_2\text{Ph}][\text{RhCl}_4]^-$	50	4.5	
Si	$[\text{Et}_3\text{N}^+\text{CH}_2\text{Ph}][\text{RhCl}_4]^-$	100	56	73/21/6/0
Si	$\text{trans-}[\text{Rh}(\text{o-phen})_2\text{Cl}_2]^+\text{Cl}^-$	50	5	
Si	$\text{trans-}[\text{Rh}(\text{o-phen})_2\text{Cl}_2]^+\text{Cl}^-$	100	10	
Si	$\text{trans-}[\text{Rh}(\text{bipy})_2\text{Cl}_2]^+\text{Cl}^-$	50	0	
Si	$\text{trans-}[\text{Rh}(\text{bipy})_2\text{Cl}_2]^+\text{Cl}^-$	100	4	
C	$\text{RhCl}(\text{PPh}_3)_3$	50	96	89.5/5/4/1.5
C	$\text{RhCl}_3 \cdot 4\text{H}_2\text{O}$	50	91	84/7.5/5.5/3
C	$[(\text{P})\text{-CH}_2\text{P}^+\text{Bu}_3][\text{RhCl}_4]^-$	50	86	89/3.5/6/1.5

thienyl)silane in the presence of these catalysts at 50°C for 6 h, the reaction yields being 93 and 91%, respectively; in the reaction with t-butylacetylene the yield was also high (96 and 91%). Catalysts on polymeric supports $[(\text{P})\text{-CH}_2\text{P}^+\text{Bu}_3][\text{RhCl}_4]^-$ and $[\text{Et}_3\text{N}^+\text{CH}_2\text{Ph}][\text{RhCl}_4]^-$ were less active whereas the rhodium-containing compounds $\text{trans-}[\text{Rh}(\text{o-phen})_2\text{Cl}_2]^+\text{Cl}^-$ and $\text{trans-}[\text{Rh}(\text{bipy})_2\text{Cl}_2]^+\text{Cl}^-$ were inactive at 50 and 100°C .

The comparison of products obtained in the reaction between dimethyl(2-thienyl)silane and trimethylethynylsilane shows a certain dependence on the nature of the rhodium catalyst. The condensation product III was obtained in highest yield

Table 6

Mass spectroscopic data for Ia–Id, IIa–IIId, IIIa, IIIb, IVa, and IVb compounds

Compound	m/z (intensity, % of the maximum)
Ia	224(M^+ , 30), 209(50), 167(20), 141(100), 127(40), 73(22), 59(20), 43(22)
IIa	224(M^+ , 10), 209(20), 141(100)
IIIa	222(M^+ , 20), 207(100), 165(20)
IVa	226(M^+ , 8), 141(100)
Ib	240(M^+ , 18), 225(30), 141(100), 73(35), 28(20)
IIb	240(M^+ , 15), 225(30), 167(30), 141(100), 73(90), 45(30)
IIIb	238(M^+ , 22), 223(100), 73(18)
IVb	242(M^+ , 8), 225(30), 167(30), 141(100), 73(90), 45(30)
Ic	300(M^+ , 8), 141(100)
IIc	267(22), 183(30), 141(100), 111(40), 43(35)
Id	330(M^+ , 18), 301(20), 257(35), 203(35), 163(60), 141(100), 119(50), 90(25), 79(75), 63(35), 45(50), 29(45)
IIId	315($M^+ - \text{Me}$, 100), 246(30), 203(20), 159(20), 141(65), 119(35), 97(35), 79(42), 45(45), 29(52)

with $\text{RhCl}(\text{PPh}_3)_3$ as catalyst. Its formation was confirmed by GC/MS (Table 6) and ^{13}C NMR data ($\delta(^{13}\text{C})$) for the carbon nuclei of the $\text{C}\equiv\text{C}$ group are 110.8 and 116.3 ppm). A product of hydrogenation of the double bond (m/z 242, M^+) was obtained in 1 and 3% yield on $\text{RhCl}_3 \cdot 4\text{H}_2\text{O}$ and $[(\text{P})\text{-CH}_2\text{PBU}_3][\text{RhCl}_4]^-$ catalysts.

The reaction of hydrosilane and t-butylacetylene on the most active rhodium catalysts affords in all cases a mixture of four products (see Table 5).

Experimental

^1H and ^{13}C NMR spectra were recorded on a Bruker WH-90/DS (90 MHz) and WH-360 (360, 90.5 MHz) spectrometer in CDCl_3 with TMS as internal standard. Mass spectra were recorded on a Kratos MS-25 apparatus (70 eV). Chromatographic analysis of mixtures was carried out with a Varian, model 3700 chromatograph using a glass column (1.2 m in length, 3 mm inner diameter) packed with 5% OV-17 Chromosorb W-HP. The temperature of the sample injector and flame-ionization detector was 250°C , the temperature of the glass column was increased in the course of the analysis from 80 to 250°C ($10 \text{ deg}/\text{min}$).

$\text{RhCl}_3 \cdot 4\text{H}_2\text{O}$, $\text{RhCl}(\text{PPh}_3)_3$ (Fluka), $[(\text{P})\text{-CH}_2\text{PBU}_3][\text{RhCl}_4]^-$ [10], $[\text{Et}_3\text{N}^+\text{CH}_2\text{-Ph}][\text{RhCl}_4]^-$ [10], *trans*- $[\text{Rh}(\text{o-phen})_2\text{Cl}_2]^+ \text{Cl}^-$ [11], *trans*- $[\text{Rh}(\text{bipy})_2\text{Cl}_2]^+ \text{Cl}^-$ [11] in the solid state ($2.5 \times 10^{-6} \text{ M}$ per 2.5 mmol of the starting silane), 0.1 M $\text{H}_2\text{PtCl}_6 \cdot 4\text{H}_2\text{O}$ in propan-2-ol were used as catalysts.

The hydrosilylation reaction was carried out in Pierce-reaction vials at 50 and 100°C . Speier's catalyst ($1.7 \times 10^{-7} \text{ M}$) or rhodium catalyst ($2.5 \times 10^{-6} \text{ M}$) was added to a mixture of 2.5 mmol of hydrosilane and 2.5 mmol of ethynylsilane followed by heating for 6 h. The ratio and structure of products in the reaction mixture were determined by GC. Similarly the corresponding silatranes were obtained by the hydrosilylation of ethynylsilatrane with phenyl- and thienyl-silane in the presence of Speier's catalyst in 3 ml of benzene (Table 1).

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