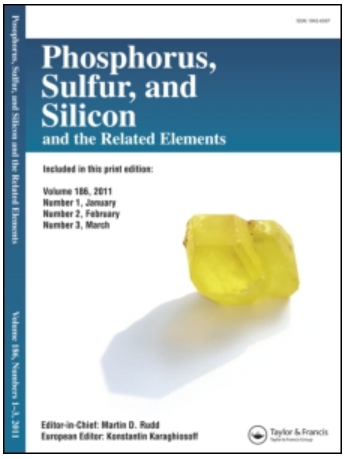

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SYNTHESIS OF ALKENYNYL VINYL SILANES

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The diethyl (3-dimethylvinylsilyl-2-propyn-1-yl)phosphonate (**2**) and (3-dimethylvinylsilyl-2-propyn-1-yl)diphenylphosphine oxide (**3**) were synthesized from 3-chloro-1-dimethylvinylsilylpropyne. Both synthons were applied in the reactions with carbonyl compounds.

Keywords: Diethyl (3-dimethylvinylsilyl-2-propyn-1-yl)phosphonate; (3-dimethylvinylsilyl-2-propyn-1-yl) diphenylphosphine oxide; synthesis; Horner-Wittig reaction; Horner-Wadsworth-Emmons reaction

INTRODUCTION

In our last papers we described the synthesis of some phosphonates[1] and diphenylphosphine oxides[2] with eight carbon atoms alkenyl units. We also demonstrated their usefulness in the Horner-Wittig reactions. Being interested in the methods of the introduction of silicon into carbon chain, especially isoprenoid, we have recogenized that the Horner-Wittig reaction can be helpful also for this purpose. Trimethylsilylpropargyl phosphonium salts or posphonates have been already used for a synthesis of eneyne silanes and after deprotection of final eneynes[3,4]. We synthesized (3-dimethylvinylsilyl-2-propyn-1-yl)diphenylphosphine oxide and (3-dimethylvinylsilyl-2-propyn-1-yl) phosphonates in order to use them as synthons for the Horner-Wittig or Horner-Wadsworth-Emmans reaction

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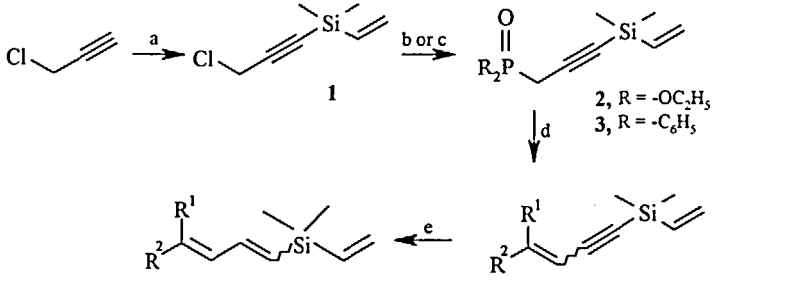
with carbonyl compounds. We expected to obtain polyene silanes which can be useful for organic synthesis. The presence of a vinyl group at the silicon in our synthons produces a possibility for further functionalization of polyene silanes to e.g. β-silanols[5]. The polyene silanes can be also a good starting material for a synthesis of cyclic silanes and polymers.

RESULTS AND DISCUSSION

Diethyl (3-dimethylvinylsilyl-2-propyn-1-yl)phosphonate (**2**) and (3-dimethyl-vinylsilyl-2-propyn-1-yl)diphenylphosphine oxide (**3**) were obtained by the reaction of 3-chloro-1-(dimethylvinylsilyl)propyne (**1**) with triethyl phosphite or methoxydiphenylphosphine respectively. 3-Chloro-1-(dimethylvinylsilyl)-propyne (**1**) was synthesized in good yield (90%) by silylation of lithium 3-chloropropynylide with dimethylvinylchlorosilane (Scheme 1).



a) 1. n-BuLi, Et_2O, -78°C. 2. $ClSi(CH_3)_2CH{=}CH_2$. b) $(EtO)_3P$, NaI. 120-130°C.
c) $(C_6H_5)_2POCH_3$, NaI. 110°C. d) $KN(SiMe_3)_2$. $R^1R^2C{=}O$. THF. -78°C→room temp.
e) i-Bu_2AlH

Both phosphonate **2** and phosphine oxide **3** were applied as synthons in the Horner-Wadsworth-Emmans and Horner-Wittig reaction respectively.

Two aldehydes (hexanal and benzaldehyde) and three ketones (acetone, cyclohexanone and 6-methyl-5-hepten-2-one) were used as carbonyl substrates. Potassium hexamethyl disilazide (KHMDS) (potassium bis (trimethylsilyl)amide) was used as a base for anion generation[6]. The condensation of ylides from phosphonate with carbonyl compounds was carried out at –78°C and the elimination of the betain formed at room temperature .In the reaction with phosphine oxide (**3**) both steps were carried out at –78°C. Generally the yields of reactions carried out with phosphine oxide (**3**) or phosphonate (**2**) were similar. The sila polyeneynes derived from cyclohexanone and 6-methyl-5-hepten-2-one were obtained in the best yields. The reactions of both aldehyds and 6-metyl-5-hepten-2-one with both synthones (**2** and **3**) afforded mixtures of isomeric sila polyeneynes as products. The isomers E decidedly predominated (70–80%) in these mixtures. Slightly better stereoselectivity was observed for reactions when the phosphine oxide **3** was applied. Trials of separation of mixtures of isomers by column chromatography afforded only pure E isomers of **4** and **5**. We tried also to transform the triple bond into a double bond. We have already applied diisobutylaluminium hydride for the reduction. The reduction of **7** gave in 77% yield a mixture of products with content 33% of E and 30% of Z isomers of the corresponding triene silane. We could not separate pure isomers from this mixture .

EXPERIMENTAL

Dimethylvinylchlorosilane, potassium bis(trimethylsilyl)amide and diisobutylaluminium hydride were purchesed from Fluka. Methoxydipheyl-phosphine was synthesized from diphenylchlorophosphine and methanol. ^{1}H NMR spectra were measured for solutions($CDCl_3$) on a Bruker Avance DRX 300 spectrometer. IR spectra were recorded on a Specord H-80 spectrophotometr. Gas chromatographic analyses were performed on a Hewlett-Packard instrument, using HP-1 capillary column (30 m × 0,31 mm). Analytical TLC was carried out on silica gel G (Merck) with different developing systems. Compounds were detected by I_2 in the iodine chamber. Column chromatography was performed on silica gel (Kieselgel 60, 230–400 mesh, Merck) with hexane and petroleum ether-acetone mixture as eluents.

3-Chloro- 1-(dimethylvinylsilyl)-propyne (1)

n-Butyl lithium (62.5 ml of 1.6M hexane solution, 0.1 mol) was added carefully through a syringe to a cooled (-78°C) solution of propargyl bromide (7.3 ml, 0.1 mol) in ethyl ether (50 ml). After stirring for 10 min dimethylvinylchlorosilane (13.9 ml, 0.1 mol) was added. The reaction mixture was stirred for 1 h allowing it to warm to room temperature. Then the mixture was quenched with a saturated solution of NH_4Cl and the product was extracted with ethyl ether. The extract was washed with brine and dried ($MgSO_4$). The crude product was distilled *in vacuo*(68°C/ 17 mmHg) to give 14,4 g (90% yield) of pure chlorosilane **1**.n^{20}_D = 1.4666, ^{1}H NMR (δ): 0.23 (s, 6H, -Si(C$\underline{H}_3$)$_2$-), 4.12 (s, 2H, -C$\underline{H}_2$Cl), 5.82 (dd, J=18.8 and 4.9 Hz, 1H, -CH=C$\underline{H}_2$, trans), 6.00 (dd, J=14.4 and 4.9 Hz, 1H, -CH=C$\underline{H}_2$ cis), 6.19 (dd, J=18.8 and 14.4 Hz, 1H, -C$\underline{H}$=CH$_2$); IR (cm^{-1}): 3056 (m), 2184 (m), 1404 (m), 1256 (s), 824 (s), 784 (s).

Diethyl (3-dimethylvinylsilyl-2-propyn-1-yl) phosphonate (2)

A mixture of triethylphosphite (9.3 ml, 0.053 mol), chloride **1** (7.9 g, 0.05 mol) and sodium iodide (0.75 g) was heated at 120–130°C for 4 h. The crude product was purified by column chromatography (silica gel, petroleum ether-acetone, 5:1). Phosphonate **2** obtained (10.6 g, 80% yield) as an oil had the following spectral data: ^{1}H NMR (δ), 0.14 (s, 6H, -Si(C$\underline{H}_3$)$_2$-), 1.28 (t, J = 6.9 Hz, 6H, -OCH$_2$C$\underline{H}_3$), 2.75(d, J= 22.2 Hz, 2H, -C$\underline{H}_2$-P-), 4.12 (q, J = 6.9 Hz, 4H, -OC$\underline{H}_2$CH$_3$), 5.77 (dd, J = 19.1 and 4.7 Hz, -CH=C$\underline{H}_2$, trans), 5.92 (dd, J = 14.5 and 4.7 Hz, 1H, - CH=C$\underline{H}_2$, cis) 6.03 (dd, J = 19.1 and 14.5 Hz, 1H, -C$\underline{H}$=CH$_2$); IR (cm^{-1}): 3048 (s), 2184 (s), 1260 (s), 1164 (m(, 1028 (s), 824 (s). Anal. Calcd. for $C_{11}H_{21}O_3PSi$: C, 50.74; H, 8.13; P, 11.90;.Found: C, 51.02; H, 8.08; P, 11.74.

Diphenyl (3-dimethylvinylsilyl-2-propyn-1-yl) phosphine oxide (3)

A mixture of methoxydiphenylphosphine (11.5 g, 0.053 mol), chloride **1** (7.9 g, 0.05 mol) and sodium iodide (0.075 g) was heated at 110°C for 1h. The crude product was purified by column chromatography (silica gel, petroleum ether-acetone, 3:1). Sila-phosphine oxide **3** was obtained (12.6 g, 78% yield) as a light - yellow oil: ^{1}H NMR (δ): 0.06 (s, 6H, -Si(C$\underline{H}_3$)$_2$-), 3.26 (d, J=17.2 Hz, 2H, - C$\underline{H}_2$C≡), 5.61 (dd, J=18.1 and 5.7 Hz, 1H, -CH=C$\underline{H}_2$, trans), 5.87 (dd, J=14.4 and 5.7 Hz, 1H, -CH=C$\underline{H}_2$, cis), 5.95 (dd, J=18.1 and 14.4 Hz, 1H, -C$\underline{H}$=CH$_2$); IR (cm^{-1}): 3056 (m),

2176 (s), 1440 (s), 1248 (m), 1204 (s), 824 (s). Anal. Calcd. for $C_{19}H_{21}OPSi$: C, 70.34; H, 6.52; P, 9.55. Found: C, 70.21; H, 6.52; P, 9.43.

Syntheses of polyene silanes (4–8)

General procedure: To a cooled (-78°C) and stirred solution of phosphonate **2** (0.004 mol) or phosphine oxide **3** (0.004 mol) in tetrahydrofuran (50 ml) - toluene solution (15 %) of KN $(SiMe_3)_2$ (0.004 mol) were added after 10 min the appropriate carbonyl compound (0.0035 mol) in tetrahydrofuran (10 ml). The reaction mixture, after 15 min, was slowly (1 h) warmed up to room temperature. When the reaction was completed the mixture was diluted with ethyl ether (100 ml) and the reaction was quenched with water (20 ml). The reaction with phosphine oxide was quenched at –78°C. The organic layer was separated and the product was extracted with ether (2 × 20 ml). The ethereal solution was washed with brine and dried ($MgSO_4$). The crude product was purified by column chromatography (silica gel, hexane). The reaction yields, physical and spectral data of polyene silanes obtained are given in the Table I.

Mixture of (E) and (Z) (3-cyclohexylidene-propenyl) dimethylvinylsilane (9)

Diisobutylaluminium hydride (1,5 ml of 1,5 M solution in hexane, 0,0015 mol) was added to silane[7] (0,2 g, 0,001 mol) in hexane (20 ml) and the reaction mixture was stirred at room temperature for 4 h. Then the mixture was diluted with ethyl ether (30 ml) washed with brine and dried ($MgSO_4$). The crude product (0.15 g, yield 77%) was purified by column chromatography (silica gel, hexene). The mixture of E (52%) and Z (48%) isomers was isolated.

^{1}H NMR (δ) :0.13 and 10.20 (two s, 6H, -Si$(CH_3)_2$ -, E and Z isomers respectively), 1.51 (m, 6H, (-$(CH_2)_3$), 2.14 and 2.30 (two m, 4H, -$(CH_2)_2$ C=), 5.43 (d, J=14.0Hz, 1H, =CH-CH=C<u>H</u>-Si$(CH_3)_2$, isomer Z), 5.69 (d, J=18.1 Hz, 1H, =CH-CH=C<u>H</u>-Si$(CH_3)_2$ -, isomer E), 5.71 (dd, J=20.1 and 8.0 Hz, 1H, -CH=C<u>H</u>$_2$, trans), 5.81 (dd, J=10.5 Hz, 1H, =C<u>H</u>-CH=CH-Si$(CH_3)_2$ -, E), 5.95 (dd, J=14.7 and 8.0 Hz, 1H, -CH=C<u>H</u>$_2$, cis), 6.00 (d, J=11.5Hz, =C<u>H</u>-CH=CH-Si$(CH_3)_2$ -, Z), 6.14 and 6.22 (two dd, J=20.1 and 14.7 Hz, 1H, -C<u>H</u>=CH$_2$), 6.82 (dd, J=18.1 and 10.5 Hz, 1H, =CH-C<u>H</u>=CH-Si$(CH_3)_2$-, E), 7.12 (dd, J=14.0 and 11.5 Hz, 1H, =CH-C<u>H</u>=CH-Si$(CH_3)_2$-, Z); IR (cm^{-1}): 3040 (w), 1640 s), 1448 (s), 1404 (m), 1248 (s), 984 (m), 972 (s), 836 (s), 696 (m).

TABLE I Physical and spectral data of polyene silanes 4–8

Compound	*Yield % Z: E Method with*		*Elemental anal. %*		n_D^{20}	*^1H NMR ($CDCl_3$) δ, J (Hz)*	*IR ν(cm^{-1})*
	2	*3*	*Calc.*	*Found*			
4	80 24:76	78 16:84	E/Z C-75.64 H-10.75	mixture C-75.34 H-10.65	isomer E 1.4795	isomer E 0.26 (s, 6H, -Si($C\underline{H}_3$)$_2$ -), 0.87 (t, J=6.8, 3H, -$CH_2C\underline{H}_3$), 2.07 (m, 2H, -$C\underline{H}_2$-CH=), 5.48 (dt, J=16.0 and 1.5, 1H, -$CH_2C\underline{H}$=CH-), 5.82 (dd, J=19.5 and 4.3, 1H, -CH=C$\underline{H}_2$ trans), 5.99 (dd, J=14.5 and 4.3, 1H, -CH=C$\underline{H}_2$, cis), 6.13 (dd, J=19.5 and 14.5, 1H, -C$\underline{H}$=CH_2), 6.22 (dt, J=16.0 and 7.1, 1H, -$CH_2C\underline{H}$=CH-)	3048(w) 3040(w) 2136(m) 1400(m) 1248(s) 952(s) 824(s)
5	62 18:82	60 7:93	isomer C-79.18 H-7.60	E C-78.75 H-7.71	isomer E 1.5996	a isomer E 0.26 (s, 6H, -Si($C\underline{H}_3$)$_2$ -), 6.19 (d, J=16.4, 1H, -CH=C$\underline{H}$-C≡), 7.01(d, J=16.4,1H,-C$\underline{H}$=CH-C≡), 7.24–7.37 (m, 5H, -$C_6\underline{H}_5$)	isomer E 3032(w) 2168(m) 1400(m) 1248(s) 1008(s) 988(s) 952(s) 824(s)

Compound	Yield % Z: E Method with		Elemental anal. %		n_D^{20}	^1H NMR ($CDCl_3$) δ, J (Hz)	IR ν(cm^{-1})
	2	3	Calc.	Found			
6	66	67	C-73.09 H-9.82	C-72.81 H-9.75	1.5236	a 0,25 s, 6H, -Si($C\underline{H}_3$)$_2$ -), 1.78 and 1.89 (two s, 6H, -C($C\underline{H}_3$)$_2$, 5.28 (m, 1H, -C$\underline{H}$=C(CH_3)$_2$)	3048(w) 3040(w) 2152(m) 1400(s) 1248(s) 1008(s) 956(s) 824(s)
7	83	85	C-76.39 H-10.86	C-76.09 H-10.93	1.5112	a 0.23 (s, 6H, -Si($C\underline{H}_3$)-), 1.56 (m, 6H), 2.12 (m, 2H), 2.40 (m, 2H) – cyklohexane protons 5.23 (s, 1H, =C$\underline{H}$-C≡),	3048(w) 3032(w) 2152(m) 1400(s) 1248(s) 1008(s) 952(s) 840(s)

Compound	*Yield % Z: E Method with*		*Elemental anal. %*		n_D^{20}	*^1H NMR ($CDCl_3$) δ, J (Hz)*	*IR ν(cm^{-1})*
	2	*3*	*Calc.*	*Found*			
8	85	82	E/Z	mixture		a	3048(w)
	29:71	19:87	C-77.51	C-77.41		E/Z mixture	2144(m)
			H-10.41	H-10.25		0.22 (Z) and 0.24 (E) (s, 6H,	1400(m)
						-($C\underline{H}_3$)$_2$ Si-),	1392(m)
						1.58 and 1.66 (two s, 6H, ($C\underline{H}_3$)$_2$	1376(m)
						C=, E)	1248(s)
						1.60 and 1.67 (two s, 6H,	1008(s)
						($C\underline{H}_3$)$_2$C, Z),	956(s)
						1.78 (s, 3H, -C(CH_3)=, Z),	840(s)
						1.90 (s, 3H, -CC$\underline{H}_3$)=, E),	
						2.09 (m, 4H, -$C\underline{H}_2$-$C\underline{H}_2$-),	
						5.06 (m, 1H, -C$\underline{H}$=C(CH_3)$_2$, E),	
						5.13 (m, 1H, -CH=C($C\underline{H}_3$)$_2$, Z),	
						5.29 (m, 1H, -C(CH_3)=C$\underline{H}$-, Z)	
						5.31 (m, 1H, -C(CH_3)=C$\underline{H}$, E),	

[a] In description of this spectrum signals of vinyl group were omitted.

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