Russian Journal of Organic Chemistry, Vol. 38, No. 2, 2002, pp. 147–149. Translated from Zhurnal Organicheskoi Khimii, Vol. 38, No. 2, 2002, pp. 167–169.
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α-Acetylene Hydrosilanes as Hydrosilylating Agents for Terminal Arylacetylenes

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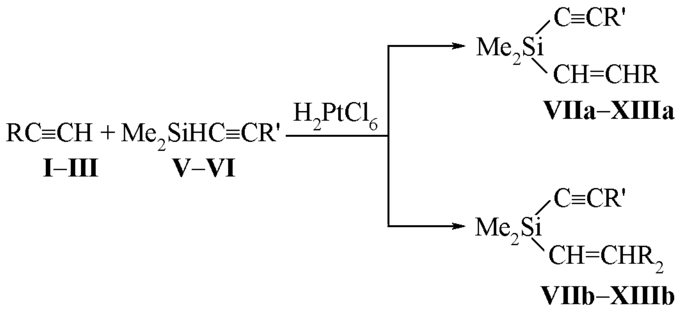
Received May 15, 2000

Abstract—The hydrosilylation of a number of acetylenes RC≡CH (R, R' = Ph, CH_2OPh, CH_2SPh) with α-ethynylhydrosilanes $Me_2SiHCH{\equiv}CR'$ in the presence of H_2PtCl_6 was investigated. The addition did not occur regioselectively, but was stereospecific and afforded a mixture of α- and trans-β-adducts. The replacement of phenyl substituent by phenoxymethyl both in the molecule of ethynylsilane and the acetylene substrate resulted in growing proportion of the α-adduct in the reaction mixture up to 10–60%.

We showed formerly [1] that 1,1-dimethylsilyl-3-phenoxy-1-propyne $Me_2SiHC{\equiv}CCH_2OPh$ in the presence of H_2PtCl_6 at ambient temperature underwent cycloautohydrosilylation to afford 1,1,4,4-tetramethyl-2,5-bis(phenoxymethyl)-1,4-disilacyclohexa-2,5-diene in 80% yield. No published data exist on application of the α-acetylene hydrosilanes as hydrosilylating agents. Yet their use in the hydrosilylation reactions of unsaturated compounds, in particular, substituted acetylenes, would provide new approaches to the synthesis of previously unknown functionally-substituted vinylethynylsilanes, promising monomers, polyfunctional reagents for the fine organic synthesis, and models for the study of silicon conjugation with multiple bonds. Obviously interesting is the study of one among fundamental hydrosilylation problems, regio and stereoselectivity of the process depending on the structure of ethynylhydrosilane and acetylene substrate.



R,R' = Ph (**I, IV, VIIa, b**), CH_2OPh (**II, V, Xa, b**), CH_2SPh (**III, VI, XIIIa, b**); R = Ph, R' = CH_2OPh (**VIIIa, b**); R = CH_2OPh, R' = Ph (**IXa, b**); R = CH_2SPh, R' = Ph (**XIa, b**); R = CH_2SPh, R' = CH_2OPh (**XIIa, b**).

In the present study was investigated the hydrosilylation of a number of monosubstituted terminal arylacetylenes of the general formula RC≡CH where R = Ph (**I**), CH_2OPh (**II**), CH_2SPh (**III**) with dimethyl(arylethynyl)silanes $Me_2SiHC{\equiv}CR'$ with R' = Ph (**IV**), CH_2OPh (**V**), CH_2SPh (**VI**). The preparation of the latter compounds we described before [2]. The reaction was carried out at 120–130°C catalyzed by chloroplatinous acid taking equimolar amounts of the reagents. As show the data of IR, ^1H, and ^{13}C NMR spectroscopy the reaction products contain *trans*- and *gem*-isomers of adducts **VIIa, b–XIIIa, b** in various ratios indicated in Table 1.

Most of monosubstituted olefins and phenylacetylene are known to take up triethylsilane under the influence of H_2PtCl_6 with prevailing orientation of silicon atom to the terminal carbon C_{sp^2} or C_{sp} giving rise to β-adducts [3–6]. With aryl propargyl ethers $HC{\equiv}CCH_2XPh$ (X = O, S) [7] and their nitrogen-containing analog, 3-oxo-1,2-benzothiazoline-2-(2'-propynyl)-1,1-dioxide [8] the similar reaction results in equal amount of regioisomers or in prevailing formation of the α-adduct (50–75%), and the fraction of the gem-isomer grows in going from X = O to X = S and then N. It was demonstrated [9] that in addition of triethylsilane to 3-substituted propynes $HC{\equiv}CCH_2X$, where X is an electron-withdrawing substituent, the amount of gem-isomers in the product could also attain 75%.

The analysis of hydrosilylation regioselectivity with respect to the nature of the acetylene substrate **I–III** and hydrosilane **IV–VI** allows some general statements. As follows from Table 1, notwithstanding the structure of ethynylhydrosilane **IV, V** the content of α-adducts **IXb, Xb** produced at orientation of the silicon atom to the substituted atom C_{sp} of 3-phen-

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Table 1. ^{1}H NMR spectra of compounds *trans*-[$Me_2Si(C{\equiv}CR')CH{=}CHR$] **VIIa**–**XIIIa** and $Me_2Si(C{\equiv}CR')CR{=}CH_2$ (*gem*) **VIIb**–**XIIIb**, δ, ppm

Compd. no.	Configuration	Isomer content, %	$Si(CH_3)_2$	SiCH=C	RCH=C	Ph	=CH_2	$OCH_2C=$, $SCH_2C=$	$OCH_2C{\equiv}C$, $SCH_2C{\equiv}C$	*J*, Hz
VIIa	*trans*	80	0.39 s	6.47 d	7.15 d	7.27–7.45 m				J_{AB} 18.0
VIIb	*gem*	20	0.33 s			7.27-7.45 m	5.86, 5.97 d.d			
VIIIa	*trans*	75	0.29 s	6.43 d	7.00 d 7.04 d	6.96–7.42 m			4.86 s	J_{AB} 19.0
VIIIb	*gem*	25	0.26 s			6.96-7.42 m	5.75, 5.90 d		4.86 s	^2J 2.1
IXa	*trans*	40	0.39 s	6.09 d.t	6.49 d.t	6.91–7.41 m		4.57 d.d		J_{AB} 18.7, $^3J_{CH_2-CH=}$ 4.0, $^4J_{CH_2C-CH}$ 1.3
IXb	*gem*	60	0.33 s			6.91–7.41 m	5.75, 5.98 m	4.75 narrow m		
Xa	*trans*	50	0.30 s	6.02 d.t	6.35 d.t	6.90–7.25 m		4.50 d.d	4.61 s	$^3J_{AB}$ 18.8, $^4J_{CH_2C-CH}$ 1.3, $^3J_{CH_2-CH=}$ 4.0
Xb	*gem*	50	0.24 s			6.90–7.25 m	5.65, 5.93 d.t	4.63	4.64	^2J 2.2, $^4J_{CH_2C-CH_2}$ 1.3
XIa	*trans*	50	0.36 s	5.71 d.t	6.24 d.t	7.40–7.22 m		3.52 d		J_{AB} 18.0 $^3J_{CH_2-CH=}$ 6.5, $^4J \approx 1.0$
XIb	*gem*	50	0.22 s			7.40–7.22 m	5.82, 5.58 narrow m	3.79 br.s		
XIIa	*trans*	65	0.30 s	5.65 d.t	6.12 d.t	6.987–7.22 m		3.52 d	4.64 s	J_{AB} 18.0, $^3J_{CH_2-CH=}$ 3.5, $^4J_{CH_2C-CH} \approx 1.0$
XIIb	*gem*	35	0.23 s			6.98–7.22 m	5.50, 5.79 m	3.70 br.s	4.64 s	
XIIIa	*trans*	40	0.30 s	5.60 d.t	6.12 d.t	7.27 m		3.58 d	3.65 s	J_{AB} 18.0, $^3J_{CH_2-CH=}$ 3.5, $^4J_{CH_2C-CH}$ 0.7
XIIIb	*gem*	60	0.26 s			7.27 m	5.48, 5.79 narrow m	3.58 s	3.58 s	

oxy-2-propyne (**II**) is by 25–30% higher than that of adducts **VIIb** and **VIIIb** formed from phenylacetylene (**I**). As concerns the effect of the ethynylhydrosilane structure on the hydrosilylation of arylacetylenes **I** and **III** we note that replacement of the phenyl substituent in hydrosilane **IV** by phenoxymethyl in **V** or phenylthiomethyl in **VI** also results in the growth of the α-adduct fraction by 10–25%. A considerable increase in the fraction of the α-adduct is observed also in going from oxygen as heteroatom in hydrosilane **V** to sulfur in hydrosilane **VI** (from 25 to 50%, phenylacetylene substrate). The maximum content of the α-adduct (60%) was observed in two cases: at R = R' = CH_2SPh (**XIIIb**), and at R = CH_2OPh, R' = Ph (**IXb**).

As seen from Table 1, the addition of hydrosilanes with silicon orientation to the terminal atom C_{sp} of the substrate occurs stereoselectively giving rise to *trans*-adducts **VIIa**–**XIIIa**.

Table 2. IR spectra of compounds $Me_2Si(C{\equiv}CR')CH{=}CHR$ **VIIa**–**XIIIa** and $Me_2Si(C{\equiv}CR')CR{=}CH_2$ **VIIb**–**XIIIb**

Compd. no.	$\nu(C{=}C)$, cm^{-1}	$\delta({=}CH_2)$, cm^{-1}	$\nu(Ph)$, cm^{-1}	$\nu(C{\equiv}C)$, cm^{-1}
VIIa, b	1560	965	1570, 1585	2140
VIIIa, b	1570	980	1590, 1600	2170
IXa,b	1580	970	1570, 1590	2160
Xa, b	1580	990	1590, 1600	2170
XIa, b	1570	960	1580, 1600	2140
XIIa, b	1570	980	1580, 1600	2140
XIIIa, b	1560	1010	1580, 1600	2170

The IR spectra of compounds obtained are presented in Table 2. They contain strong absorption bands from stretching vibrations of the triple bond adjacent to silicon atom in the region 2140–2170 cm^{-1}, stretching vibrations of the $C{=}C$ bond in the range 1560–1580 cm^{-1}; to the bending vibrations of C–H bond from the $=CH_2$ group belong the bands at 965–1010 cm^{-1}. No absorption bands in the products from the stretching vibrations of the Si–H bond evidenced the completion of the process. We described formerly in the IR spectra of α-ethynylhydrosilanes the presence of two absorption bands in the region 2044–2153 cm^{-1} corresponding to the stretching vibrations of the Si–H and triple bonds [2].

EXPERIMENTAL

^1H NMR spectra were recorded on spectrometer JEOL FX-90Q, operating frequency 80 MHz, solvent $CDCl_3$, internal reference cyclohexane. IR spectra were registered on spectrophotometer Specord 75IR from thin films (0.025 cm).

Reaction of 1-dimethylsilyl-3-phenoxy-1-propyne (V) with 3-phenoxy-1-propyne (II). A mixture of 3-phenoxy-1-propyne (6.6 g, 0.05 mol) and 0.01 ml of Spyer's catalyst (0.1 M solution of $H_2PtCl_6 \rightarrow H_2O$ in 2-propanol) was heated to 80°C, and slowly, within 1 h, was added dropwise 9.5 g (0.05 mol) of hydrosilane **V**. The reaction mixture was heated to 120–130°C for 6 h. We obtained 16,1 of viscous reaction product. Found, %: C 74.15; H 6.85; Si 8.88. $C_{20}H_{22}O_2Si$. Calculated, %: C 73.92; H 6.70; Si 8.60. According to ^1H NMR data the product was a mixture of regioisomers 1'-(3'-phenoxy-1'-propynyl)-1-(3'-phenoxy-1'-propynyl)-1,1-dimethylsilane (**Xa**) and 1-(3-phenoxy-2-propynyl)-1-(2-phenoxymethyl-2-ethenyl)-1,1-dimethylsilane (**Xb**) in a ratio 40 : 60 (Table 1). The reactions of acetylene substrates **I, III** with hydrosilanes **IV, VI** were carried out in the same way. No bands from the Si–H bond both in IR and ^1H NMR spectra indicated that the initial hydrosilane reacted completely.

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