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Dedicated to Full Member of the Russian Academy of Sciences B.A. Trofimov on the 65th Anniversary of His Birth

Hydrosilylation of 2-(2-Propynyl)-2,3-dihydro-1,2-benzothiazol-3-one 1,1-Dioxide with 1-Alkynyl(dimethyl)- and Bis(1-alkynyl)methylsilanes

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Abstract—Hydrosilylation of 2-(2-propynyl)-2,3-dihydro-1,2-benzothiazol-3-one 1,1-dioxide with 1-alkynyldimethyl- and bis(1-alkynyl)methylsilanes of the general formula $Me_nHSi(C{\equiv}CR)_{3-n}$ (n = 1, 2) in the presence of H_2PtCl_6 (Speier's catalyst) occurs in a nonregioselective but stereoselective fashion, yielding mixtures of the corresponding *trans*-β- and α-adducts. The fraction of the latter ranges from 50 to 70%, depending mainly on the substrate nature rather than on the nature of substituent at the triple bond of the reagent.

Hydrosilylation of triple C≡C bond underlies one of the main methods for synthesizing vinylsilanes which are widely used in the preparation of polymers [1], their modification [2–4], and synthesis of natural compounds [5]. Acetylenic silicon hydrides have poorly been studied as hydrosilylating agents, though introduction of an alkynyl group to the silicon atom in vinylsilanes should extend their potential as ligands for metal-complex catalysis, promising monomers, polyfunctional reagents for fine organic synthesis, and model structures for studying conjugation between the silicon heteroatom and multiple bonds.

We previously studied autohydrosilylation of 1-(dimethylsilyl)-3-phenoxypropyne $Me_2HSiC{\equiv}CCH_2OPh$ in the presence of H_2PtCl_6 at room temperature, which led to formation of 1,1,4,4-tetramethyl-2,5-bis(phenoxymethyl)-1,4-disila-2,5-cyclohexadiene in high yield [6], and hydrosilylation of a series of terminal arylacetylenes RC≡CH (R = Ph, $PhOCH_2$, $PhSCH_2$) with ethynylsilanes in the presence of Speier's catalyst [7]. There are no published data on the use of bis(1-alkynyl)silanes as hydrosilylating agents, as well as on hydrosilylation with ethynylsilanes of nitrogen-containing heterocycles having a 2-propynyl group on the nitrogen, specifically of 2-(2-propynyl)-2,3-dihydro-1,2-benzothiazol-3-one 1,1-dioxide (**I**) which was synthesized by us previously [8]. We anticipated that hydrosilylation of compound **I** with mono- and bis-acetylenic silicon hydrides will give rise to new polyfunctional vinyl(ethynyl)silanes possessing a pharmacophoric group. For example, some biologically active benzothiazole derivatives are promising for the treatment of pulmonal emphysema [9, 10].

The relations between the structure of silicon hydride and stereo- and regioselectivity of triple bond hydrosilylation have been studied insufficiently. Chauhan *et al.* [11] recently showed a considerable effect of the structure of chloro-, alkyl-, and alkoxysilanes on the regio- and stereoselectivity of their addition to terminal and internal alkynes, catalyzed by platinum on charcoal.

In the present work we examined hydrosilylation of compound **I** with 1-alkynylsilanes **II**–**IX** of the general formula $Me_nSiH(C{\equiv}CR)_{3-n}$, where n = 1, 2; R = Me_3Si, Et_3Ge, Ph, $PhOCH_2$, $PhSCH_2$. The synthesis of silanes **II**–**VII** and **IX** was reported by us previously [12], and methylbis(triethylgermylethynyl)silane (**VIII**) was obtained in 67% yield by reaction of dichloro(methyl)silane with triethylgermylethynylmagnesium bromide in THF. The hydrosilylation was carried out with equimolar amounts of the reactants in THF at 70°C in the presence of Speier's catalyst.

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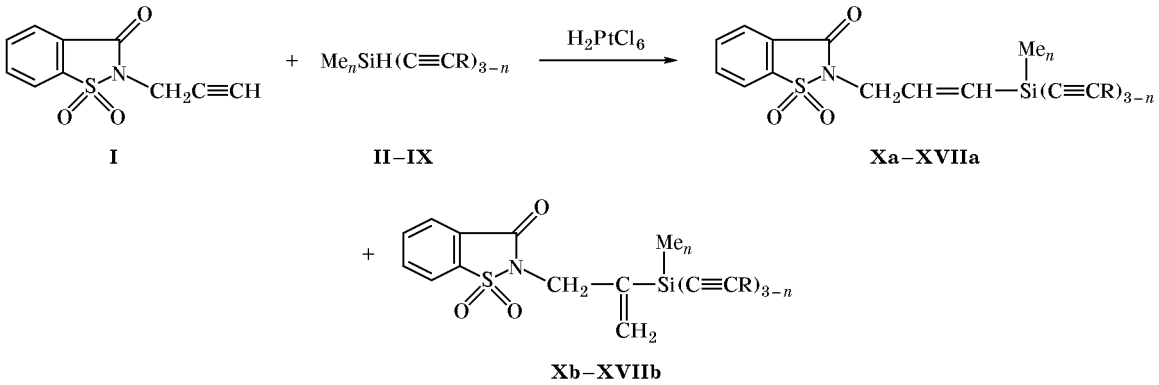
Scheme 1.



I **II–IX** **Xa–XVIIa**

Xb–XVIIb

II, **Xa**, **Xb**, R = Me_3Si, *n* = 2; **III**, **XIa**, **XIb**, R = Et_3Ge, *n* = 2; **IV**, **XIIa**, **XIIb**, R = Ph, *n* = 2; **V**, **XIIIa**, **XIIIb**, R = $PhOCH_2$, *n* = 2; **VI**, **XIVa**, **XIVb**, R = $PhSCH_2$, *n* = 2; **VII**, **XVa**, **XVb**, R = Me_3Si, *n* = 1; **VIII**, **XVIa**, **XVIb**, R = Et_3Ge, *n* = 1; **IX**, **XVIIa**, **XVIIb**, R = Ph, *n* = 1.

According to the IR and ^1H and ^{13}C NMR data, in all cases mixtures of regioisomeric *trans*-β- and α-adducts **Xa**–**XVIIa** and **Xb**–**XVIIb** were formed; their ratios and ^1H NMR spectral parameters are given in table. We previously showed [7] that the addition of ethynylsilanes $Me_2HSiC{\equiv}CR$ (R = Ph, $PhOCH_2$, $PhSCH_2$) to arylacetylenes in the presence of H_2PtCl_6 is not regioselective, but the corresponding β-adducts are formed with high *trans*-stereoselectivity. A strong effect of the substrate structure on the ratio of the α- and β-adducts was observed: the fraction of the former increases on replacement of phenyl group by phenoxy or phenylsulfanylmethyl both in the substrate and in the ethynylsilane (the fraction of the α-adduct ranges from 10 to 60%). The predominant formation of the α-adduct (up to 75%) was also observed in the hydrosilylation of **I** with triethylsilane under similar conditions [8].

Presumably, the presence of electron-acceptor triple bond in the hydrosilylating agent should increase

^1H NMR spectra of compounds **Xa**–**XVIIa** and **Xb**–**XVIIb**

Comp. no.	Fraction, %	$Si(CH_3)_2$	NCH_2	C=CHSi or $=CH_2$	$=CHCH_2$	H_{arom}	*J*, Hz
Xa	40	0.25 s	4.43 d.d	6.04 d.t	6.30 d.t	7.8–8.1 m	^3J = 5.3, ^4J = 1.5, ^tJ = 18.4
Xb	60	0.37 s	4.54 t	5.70–5.90 q			^2J = ^4J = 1.6
XIa	40	0.24 s	4.41 d.d	6.02 d.t	6.30 d.t	6.7–8.0 m	^3J = 5.3, ^4J = 1.5, ^tJ = 18.5,
XIb	60	0.35 s	4.53 d.d	5.71–5.87 m			^2J = ^4J = 1.5
XIIa	35	0.27 s	4.43 m	6.01 d.t	6.35 d.t	7.0–8.1 m	^3J = 5.3, ^4J = 1.5, ^tJ = 18.5
XIIb	65	0.40 s	4.50 t	5.73–5.94 m			
XIIIa[a]	50	0.24 s	4.40 d.d	6.02 d.t	6.27 d.t	6.7–8.0 m	^3J = 5.3, ^4J = 1.5, ^tJ = 18.5
XIIIb	50	0.35 s	4.69 m	5.68–5.91 m			
XIVa[b]	45	0.15 s	4.39 d.d	5.97 d.t	6.20 d.t	7.9–8.04 m	^3J = 5.3, ^4J = 1.5, ^tJ = 18.5
XIVb	55	0.28 s	4.44 d.d	5.61–5.85 t			
XVa	30	0.40 s	4.45 d.d	5.99 d.t	6.46 d.t	7.8–8.1 m	^3J = 5.2, ^4J = 1.6, ^tJ = 18.4
XVb	70	0.50 s	4.49 t	5.89–5.94 d.t			
XVIa	40	0.37 s	4.43 d.d	6.02 d.t	6.48 d.t	7.8–8.1 m	^3J = 5.2, ^4J = 1.6, ^tJ = 18.5
XVIb	60	0.49 s	4.62 t	5.89 br.t			
XVIIa	50	0.54 s	4.51 t	6.15 d.t	6.60 d.t	7.0–8.1 m	^3J = 5.2, ^4J = 1.6, ^tJ = 18.5
XVIIb	50	0.66 s	4.72 t	6.03–6.04 m			

[a] $\delta(OCH_2)$, ppm: 4.63 s (**XIIIa**); 4.66 (**XIIIb**).

[b] $\delta(SCH_2)$, ppm: 3.61 s (**XIVa**); 3.58 s (**XIVb**).

positive charge on the silicon atom thus favoring its orientation at the α-carbon atom at the triple bond of the substrate. As a result, the corresponding α-adduct should be formed as the major product. As follows from the data given in table, the addition of silanes **II**–**IX** actually gives a considerable amount of α-adducts **Xb**–**XVIIb** whose fraction reaches 50–70%. Comparison of the isomer ratio in the hydrosilylation products obtained with trimethylsilyl- and trimethylgermylethynylsilanes **II** and **III**, on the one hand, and bis(ethynyl) analogs **VII** and **VIII**, on the other, shows increased fraction of bis(ethynyl) α-adduct **XVb** (by 10%). On the other hand, the fraction of α-adduct **XIIb** in the reaction with silane **IV** (R = Ph, n = 2) is larger by 15% than the fraction of the corresponding bis(phenylethynyl) analog **XVIIb**. These data indicate the absence of clearly defined difference between mono- and bis(ethynyl)silanes in the regioselectivity of addition to compound **I**. The effect of the substituent at the triple bond in the series of monoethynylsilanes **X**–**XIV** is also insignificant: the fraction of the α-adduct in the hydrosilylation products ranges from 50 to 70%.

The IR spectra of the products contain strong absorption bands due to stretching vibrations of the triple C≡C bond at 2160–2180 cm^{-1}, carbonyl group at 1720–1730 cm^{-1}, double C=CSi bond at 1620–1630 cm^{-1}, aromatic C=C bonds at 1580–1600 cm^{-1}, and Si−CH_3 bond at 1240–1250 cm^{-1}. Absorption bands of the triple bond between two heteroatoms are characterized by a considerably lower frequency: 2030 and 2090 cm^{-1} for adducts **XVIa** and **XVIb**, respectively (R = Et_3Ge, n = 1). Compounds **XVa** and **XVb** (R = Me_3Si, n = 1) show no triple bond absorption in the IR spectrum, presumably due to their pseudosymmetric structure. In the IR spectra of monoethynyl analogs **Xa** and **Xb** (R = Me_3Si), the ν(C≡C) bands appear at 2110 and 2070 cm^{-1}, and adducts **XIa** and **XIb** (R = Et_3Ge) absorb at 2100 and 2058 cm^{-1}, respectively. Appreciable reduction of the triple bond stretching vibration frequency in symmetric disilylacetylenes is well known: for example, the ν(C≡C) frequency of $Me_3SiC{\equiv}CSiMe_3$ is 2130 cm^{-1} [13]. According to Voronkov *et al.* [14], stretching vibrations of the vinyl C−H bond in vinylsilanes give rise to a sharp absorption band at 3060–3030 cm^{-1}. Insofar as stretching vibration bands of the aromatic C−H bonds are located in the same region, it was difficult to identify ν(C−H) vibrations of the $SiC{=}CH_2$ moiety in most adducts derived from benzisothiazole **I**. An exception was the IR spectrum of adduct **XIIIb** (R = CH_2OPh, n = 2), where a strong clearly defined band was present at 3060 cm^{-1}. In the IR spectra of compounds containing no phenyl ring at the triple bond, a narrow peak at 1590–1595 cm^{-1} corresponds to stretching vibrations of the C=C bonds in the benzisothiazole fragment. Phenyl-substituted adducts **XIIa**, **XIIb** (R = Ph, n = 2); **XIIIa**, **XIIIb** (R = CH_2OPh, n = 2); **XIVa**, **XIVb** (R = CH_2SPh, n = 2); and **XVIIa**, **XVIIb** (R = Ph, n = 1) each show two absorption bands in the region 1580–1600 cm^{-1}. The ^1H NMR spectra of compounds **X**–**XVII** are given in table.

Thus the results of the present study and our previous data [6–8] indicate that the regioselectivity of hydrosilylation is determined mainly by the structure of acetylenic substrate.

EXPERIMENTAL

The IR spectra of compounds **VIII**–**XVII** were obtained on a Specord 75IR spectrophotometer; samples were examined as KBr pellets or liquid films (neat). The ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX-400 instrument in $CDCl_3$ using cyclohexane as internal reference.

Methylbis(triethylgermylethynyl)silane (VIII). Triethylgermylacetylene [15], 27.69 g (0.15 mol), was added dropwise under stirring to the Grignard compound prepared from 3.6 g (0.15 mol) of magnesium and 16.3 g (0.15 mol) of ethyl bromide in 100 ml of THF. The mixture was stirred for 12 h at room temperature and then for 3 h at 65°C. It was then cooled to room temperature, and 17.25 g (0.15 mol) of dichloro(methyl)silane was added dropwise over a period of 30 min. The mixture was treated with 50 ml of 5% hydrochloric acid and extracted with diethyl ether, the extract was dried over $CaCl_2$, the solvent was removed, and the residue was distilled under reduced pressure. Yield 41.1 g (67%), bp 122°C (1 mm), n_D^{20} = 1.4848. IR spectrum, ν, cm^{-1}: 2156 (C≡C); 2100 (Si−H); 1250, 840 (Si−C). ^1H NMR spectrum, δ, ppm: 0.34 d (3H, SiMe), 0.85 q (12H, $CH_3C\mathbf{H}_2Ge$), 1.07 t (18H, $C\mathbf{H}_3CH_2Ge$), 4.29 q (1H, SiH). Found, %: C 49.67; H 8.01; Ge 34.62; Si 6.89. $C_{17}H_{34}Ge_2Si$. Calculated, %: C 49.74; H 8.35; Ge 34.91; Si 7.01.

Reaction of 2-(2-propynyl)-2,3-dihydro-1,2-benzothiazol-3-one 1,1-dioxide (I) with dimethyl(3-phenoxy-1-propynyl)silane (VIII). A mixture of 2.21 g (0.01 mol) of compound **I**, 1.9 g (0.01 mol) of silane **V**, and 0.01 ml of Speier's catalyst (a 0.1 M solution of $H_2PtCl_6 \cdot 6H_2O$ in *i*-PrOH) in 10 ml of tetrahydrofuran was stirred for 6 h at 60–65°C. The

solvent was removed, and the residue was analyzed. Found, %: C 63.45; H 5.66; N 3.90; S 8.32; Si 7.59. $C_{21}H_{21}NO_4SSi$. Calculated, %: C 61.28; H 5.14; N 3.40; S 7.79; Si 6.82.

The reactions of compound **I** with silanes **II**–**VII** and **IX** were carried out in a similar way (see table).

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