

# The photochemical reaction of Si-substituted vinyl(ethynyl)- and diethynylsilanes with ethanethiol and its C-functional derivatives

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## Abstract

The photoinitiated addition of ethanethiol and its derivatives  $XCH_2CH_2SH$  ( $X = HS-, HO-, (C_2H_5)_2N-$ ) to vinyl(ethynyl)- and diethynyl(diorganyl)silanes has been studied. The photochemical reaction of diethynyl (diorganyl)silanes with thiylation agents proceeds with participation of only one ethynyl group. In contrast to this, the double band of vinyl(ethynyl)diorganyl silanes takes part in photoinitiated thiylation. © 1999 Published by Elsevier Science S.A. All rights reserved.

**Keywords:** Photochemistry; Silanes; Ethanethiol addition

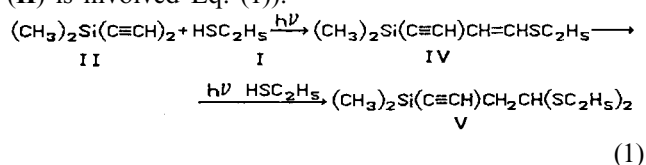
## 1. Introduction

In continuation of our systematic investigation of the photochemical thiylation of alkenyl- and ethynyl(organyl)silanes [1–3] we have studied the photoinitiated reaction of vinyl(ethynyl)- and diethynyl-(diorganyl)silanes with ethanethiol (**1a**) and its derivatives  $XCH_2CH_2SH$  (**1b**,  $X = HS-$ ; **1c**,  $X = HO-$ ; **1d**,  $X = (C_2H_5)_2N$ ).

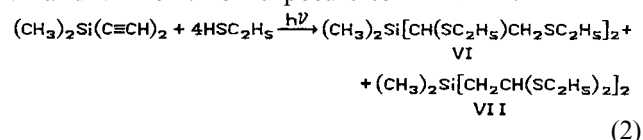
The known data about the homolytic addition of alkanethiols to organic compounds, containing both double and triple bonds, are contradictory. Some of them indicate primary addition of alkanethiols to the double bond [4], and other data to the triple bond [5]. The behaviour of isostructural organosilicon compounds in analogous reactions has not been studied so far. The synthesis of initial diethynyl(dimethyl)silane (**II**) and vinyl(ethynyl)methyl(ethyl)silane (**III**) has been described earlier [6].

## 2. Results and discussion

In the photochemical reaction of equimolar quantities of diethynyl(dimethyl)silane (**II**) and ethanethiol (**1a**) (UV-irradiation for 16 h), only one ethynyl group (**II**) is involved Eq. (1).



The conversion of diethynyl(dimethyl)silane (25%) is much lower than that for ethynyl(trimethyl)silane (90%) in this reaction. Together with the monoadduct (**IV**), the diadduct (**V**) is formed in higher yield (the yields of adducts **IV** and **V** are 5 and 37.4%, respectively). The second ethynyl group of silane (**II**) can be involved in the reaction with ethanethiol (**1a**) only at the ratio of reagents **1a** and **II** of 8:1. In this case two tetradducts (**VI** and **VII**) are formed (Eq. (2)). The ratio of adducts **VI** and **VII** is 1:2 on exposure to <sup>1</sup>H-NMR.

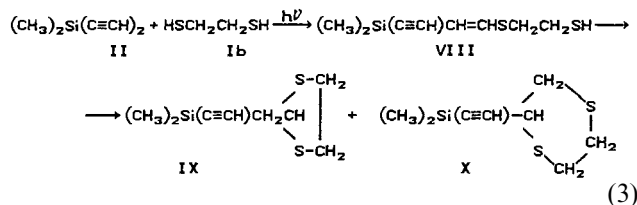


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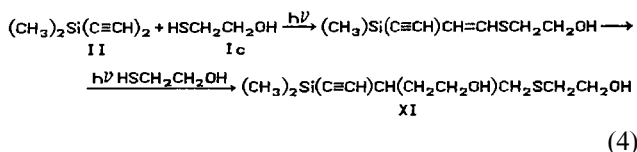
Table 1  
The physico-chemical constants, yields (%) and elemental analysis data for the adducts obtained

Adducts	Yield (%)	B.p. (°C/ mmHg)	$n_D^{20}$	Empirical formula	Elemental analyses, found/calculated (%)				
					C	H	N	S	Si
V	37.4	90/10 <sup>-1</sup>	1.5190	C <sub>10</sub> H <sub>20</sub> S <sub>2</sub> Si	51.60/51.72	8.70/8.71	–	27.59/27.59	12.07/12.11
XI	19.6	169/10 <sup>-1</sup>	–	C <sub>10</sub> H <sub>20</sub> O <sub>2</sub> S <sub>2</sub> Si	45.48/45.46	8.00/7.57	–	23.70/24.23	10.27/10.61
XII	16.7	155/10 <sup>-1</sup>	1.5006	C <sub>12</sub> H <sub>23</sub> NSSi	–	–	5.64/5.79	13.05/13.22	11.11/11.57
XIII	28.9	52/10 <sup>-1</sup>	1.4839	C <sub>9</sub> H <sub>18</sub> SSi	57.50/58.06	9.83/9.67	–	18.68/17.20	15.86/15.05
XVII	46.6	175/10 <sup>-1</sup>	1.5025	C <sub>13</sub> H <sub>30</sub> S <sub>3</sub> Si	50.34/50.32	9.97/9.67	–	30.40/30.96	9.70/9.03
XVIII mixture	15.7	97/10 <sup>-1</sup>	1.4987	C <sub>11</sub> H <sub>24</sub> S <sub>2</sub> Si	53.92/53.22	9.77/9.68	–	25.22/25.80	11.31/11.29
VI + VII mixture	52.4	180/10 <sup>-1</sup>	–	C <sub>14</sub> H <sub>32</sub> S <sub>4</sub> Si	46.82/47.19	9.09/8.99	–	35.49/35.95	8.54/7.86
IX + X	14.6	63/10 <sup>-1</sup>	–	C <sub>8</sub> H <sub>14</sub> S <sub>2</sub> Si	47.22/47.52	6.98/6.93	–	31.17/31.68	13/40/13.86

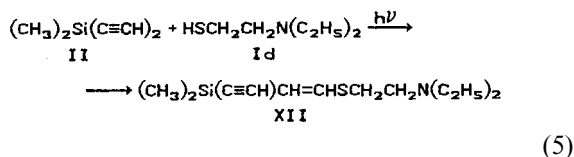
Under UV-irradiation 1,2-ethanedithiol (**Ib**) reacts with only one ethynyl group of silane (**II**) to form monoadduct (**VIII**). The intermolecular cyclization of adduct (**VIII**) leads to a mixture of organosilicon derivatives of 1,3-dithiolane (**IX**) and 1,4-dithiane (**X**) (Eq. (3)).



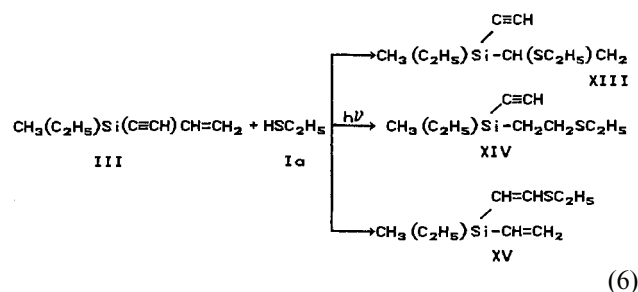
Similarly the ethanethiol derivative (**Ic**) reacts with only one ethynyl group of silane (**II**) under UV-irradiation. The  $\alpha,\beta$ -diadduct (**XI**) is the final product in this reaction (Eq. (4)). This means that the rate of thiylation of the SiCH=CHS-group is higher than that for the SiC≡CH-group.



In contrast to the thiol (**Ic**), the 2-(diethylamine)ethanethiol (**Id**) reacts with organosilicon compound (**II**) under UV-irradiation to form only  $\beta$ -monoadduct (**XII**) (yield 23%) (Eq. (5)).



So, the nature of the thiyating agent also has an essential influence on the reaction course. The double bond as well as the triple bond of vinyl(ethynyl)-methyl(ethyl)silane (**III**) takes part in the photochemical reaction with ethanethiol (UV-irradiation for 16 h) Eq. (6).



The photoinitiated addition of thiol (**Ia**) to the double bond (**III**) proceeds non-regioselectively and leads to a mixture of adducts (**XIII**) and (**XIV**) with prevalence of the former (**XIV**).

The addition of thiol (**Ia**) to the triple bond of organosilicon compound (**III**) is stereo- and regioselective and leads to the transformation of methyl(ethyl)-

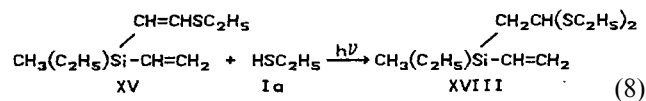
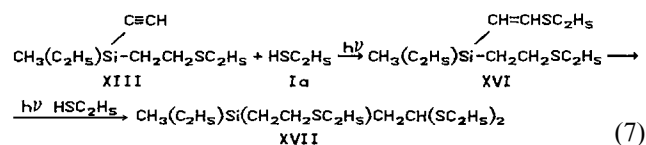
Table 2  
IR spectral data for the adducts obtained

Adduct	IR (cm <sup>-1</sup> )
V	3280s, $\nu(\text{HC}\equiv)$ , 2030, s, $\nu(\text{C}\equiv\text{CH})$ , 1250s, 800s $\nu(\text{CH}_3\text{-Si})$
Mixture of VI and VIII	2970s, 2880s, $\nu(\text{R-CH}_2\text{-R})$ , 1250s, 800s, $\nu(\text{CH}_3\text{Si})$
Mixture of IX and X	3270s, $\nu(\text{HC}\equiv)$ , 2040s, $\nu(\text{C}\equiv\text{CH})$ , 1240s, 840s, $\nu(\text{CH}_3\text{Si})$ , 770m, $\nu(\text{Si-C})$ , 610m, $\nu(\text{C-S in cycle})$
XI	3380vs, $\nu(\text{OH})$ , 3280s, $\nu(\text{C}\equiv\text{CH})$ , 2050s, $\nu(\text{C}\equiv\text{CH})$ , 860s, 730m $\nu(\text{Si-C})$
XII	3280s, $\nu(\text{HC}\equiv)$ , 2030s, $\nu(\text{C}\equiv\text{CH})$ , 1610s, $\nu(\text{C=C-S})$ , 1305m, $\nu(\text{N-C})$ , 1250s, 860s, $\nu(\text{CH}_3\text{Si})$
XIII	3280s, $\nu(\text{HC}\equiv)$ , 2080s, $\nu(\text{C}\equiv\text{CH})$ , 1255s, 800s, $\nu(\text{CH}_3\text{Si})$
XV	3050s, $\nu(\text{S-CH=})$ , 1585s, $\nu(\text{SCH=CH})$ , 1530m, $\nu(\text{SiCH=CH}_2)$ , 1255s, 800s, $\nu(\text{CH}_3\text{Si})$ , 1010s, 955s, $\delta(\text{H}_2\text{C=})$
XVI	3050s, $\nu(\text{SCH=})$ , 1590s, $\nu(\text{SCH=CH})$ , 1255s, 800s, $\nu(\text{CH}_3\text{Si})$
XVIII	1520s, $\nu(\text{SiCH=CH}_2)$ , 1255s, 850s, $\nu(\text{CH}_3\text{Si})$ , 1010s, 955s, $\delta(\text{H}_2\text{C=})$

Table 3  
<sup>1</sup>H-NMR spectra of the adducts obtained

Adducts	<sup>1</sup> H-NMR (80 MHz, CDCl <sub>3</sub> ), δ, ppm
V	0.29 (s, 6H, CH <sub>3</sub> Si), 1.25 (tr, 6H, CH <sub>3</sub> CH <sub>2</sub> S), 1.40 (d, 2H, CH <sub>2</sub> Si), 2.43 (s, 1H, C≡CH), 2.63 (m, 4H, CH <sub>3</sub> CH <sub>2</sub> S), 4.07 (tr, 1H, CH <sub>2</sub> CH)
VI	0.25 (s, 6H, CH <sub>3</sub> Si), 1.27 (tr, 6H, CH <sub>3</sub> CH <sub>2</sub> S), 2.63 (m, 4H, CH <sub>3</sub> CH <sub>2</sub> S), 3.99 (d, 2H, SiCH)
VII	0.20 (s, 6H, CH <sub>3</sub> Si), 1.27 (tr, 12H, CH <sub>3</sub> CH <sub>2</sub> S), 1.35 (d, 4H, SiCH <sub>2</sub> ), 2.63 (m, 8H, CH <sub>3</sub> CH <sub>2</sub> S), 3.99 (tr, 2H, CH <sub>2</sub> CH)
IX	0.14 (s, 6H, CH <sub>3</sub> Si), 1.37 (d, 2H, SiCH <sub>2</sub> ), 2.37 (s, 1H, C≡CH), 3.02–3.29 (m, 4H, CH <sub>2</sub> in cycle), 4.74 (m, 4H, CH <sub>2</sub> in cycle)
X	0.14 (s, 6H, CH <sub>3</sub> Si), 2.37 (s, 1H, C≡CH), 2.48 (d, 1H, SiCH), 2.69–3.02 (m, 2H, SCH <sub>2</sub> CHS), 3.02–3.29 (m, 4H, CH <sub>2</sub> in cycle)
XI	2.68 (tr, 4H, SCH <sub>2</sub> ), 2.91 (s, 1H, SiCH), 3.68 (tr, 4H, CH <sub>2</sub> O), 4.74 (s, 2H, OH)
XII	0.96 (tr, 6H, CH <sub>3</sub> CH <sub>2</sub> N), 2.67 (tr, 2H, SCH <sub>2</sub> ), 2.68 (tr, 2H, CH <sub>2</sub> N), 2.94 (m, 4H, NCH <sub>2</sub> CH <sub>3</sub> ), 5.70 (s, 1H, SiCH=)
XIII	0.10 (s, 3H, CH <sub>3</sub> Si), 0.62 (m, 2H, CH <sub>3</sub> CH <sub>2</sub> Si), 0.88 (m, 3H, CH <sub>3</sub> CH <sub>2</sub> Si), 1.18 (tr, 3H, CH <sub>3</sub> CH <sub>2</sub> S), 2.34 (s, 1H, C≡CH), 2.54 (m, 2H, CH <sub>3</sub> CH <sub>2</sub> S)
XIV	0.10 (s, 3H, CH <sub>3</sub> Si), 0.62 (m, 2H, CH <sub>3</sub> CH <sub>2</sub> Si), 0.88 (m, 3H, CH <sub>3</sub> CH <sub>2</sub> Si), 1.18 (tr, 3H, CH <sub>3</sub> CH <sub>2</sub> S), 1.52 (d, 3H, C-CH <sub>3</sub> ), 3.90 (qw, 1H, CH-CH <sub>3</sub> )
XV	5.61 (d, 1H, SiCH=), 6.00 (m, 2H, CH <sub>2</sub> =CH), 6.58 (d, 1H, S-CH=)
XVII	0.10 (s, 3H, SiCH <sub>3</sub> ), 0.67 (m, 2H, CH <sub>3</sub> CH <sub>2</sub> Si), 0.96 (m, 3H, CH <sub>3</sub> CH <sub>2</sub> Si), 1.25 (tr, 9H, CH <sub>3</sub> CH <sub>2</sub> S), 1.38 (d, 2H, CHCH <sub>2</sub> S), 2.59 (m, 8H, CH <sub>2</sub> S), 3.95 (tr, 1H, CHS)
XVIII	0.11 (s, 3H, SiCH <sub>3</sub> ), 0.66 (m, 2H, CH <sub>3</sub> CH <sub>2</sub> Si), 0.90 (m, 3H, CH <sub>3</sub> CH <sub>2</sub> Si), 1.19 (tr, 6H, CH <sub>3</sub> CH <sub>2</sub> S), 1.28 (d, 2H, SiCH <sub>2</sub> ), 2.55 (m, 4H, CH <sub>2</sub> S), 3.89 (tr, 1H, CHS), 6.00 (m, 2H, CH <sub>2</sub> =CH)

vinyl(2-ethylthiovinyl)silane (XV). It was not possible to isolate the adduct (XV) in the pure form. It was identified in the reaction mixture by <sup>1</sup>H-NMR. The reaction of organosilicon compound (III) with ethanethiol (Ia) is not limited by the formation of the adducts (XIII–XV). Besides them, the diadducts (XVI, XVIII) and triadduct (XVII), and the products of deeper thiylation of initial compound (III), are formed (Eqs (7) and (8))



The conversion of compound (III) and the yields of adducts (XV–XVIII) depend greatly on the ratio of

reagents (Ia) and (III). When this ratio is equimolar, the double bond of compound (III) is mainly involved to form the adduct (XIII) (yield 29%). The product of monoaddition of the thiol (Ia) to the triple bond of (III) is present only in traces in the reaction mixture (less than 5%). At the same time, the yield of diadduct (XVIII) is 15%. When the III:Ia ratio is 1:2, the conversion of compound (III) is 80%, the triadduct (XVII) being the main reaction product.

### 3. Experimental

<sup>1</sup>H-NMR spectra were run on Tesla-487B (80 MHz) and Jeol-FX-90 (90 MHz) spectrometers (CDCl<sub>3</sub>, HMDS). IR spectra were recorded on a UR-20 spec-

Table 4  
 Mass spectrum of the adducts obtained

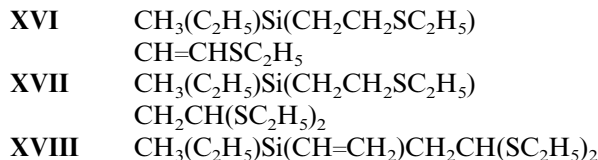
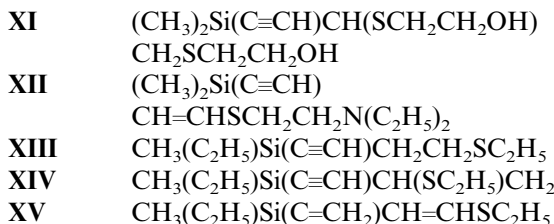
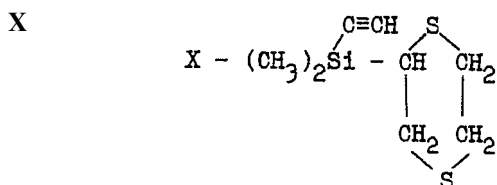
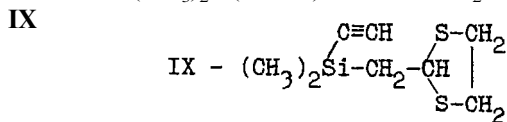
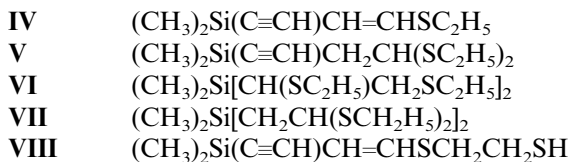
Adducts	<i>m/z</i> , relative intensity
IV	170 (M <sup>+</sup> , 33%); 155 (M-CH <sub>3</sub> , 24); 141 (M-C <sub>2</sub> H <sub>5</sub> , 52); 109 (M-SC <sub>2</sub> H <sub>5</sub> , 4); 83/(CH <sub>3</sub> ) <sub>2</sub> SiC≡CH <sup>+</sup> , 43/
V	232 (M <sup>+</sup> , 4%); 217 (M-CH <sub>3</sub> , 1); 203 (M-C <sub>2</sub> H <sub>5</sub> , 71); 171 (M-SC <sub>2</sub> H <sub>5</sub> , 16); 146/M-(HC≡C)-SC <sub>2</sub> H <sub>5</sub> , 45/; 119, /C <sub>2</sub> H <sub>5</sub> (SC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> <sup>+</sup> , 13/; 83, /(CH <sub>3</sub> ) <sub>2</sub> SiC≡CH <sup>+</sup> , 100/
VI	356 (M <sup>+</sup> , 1%); 282 (M-CH <sub>2</sub> SC <sub>2</sub> H <sub>5</sub> , 4); 206/M-C <sub>2</sub> H <sub>4</sub> (SC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> <sup>+</sup> ; 100/; 234 (M-2C <sub>2</sub> H <sub>5</sub> , 18); 192, /(CH <sub>3</sub> ) <sub>2</sub> SiCH(SC <sub>2</sub> H <sub>5</sub> )CH <sub>2</sub> SCH <sub>2</sub> <sup>+</sup> , 32/; 119, /(CH <sub>3</sub> ) <sub>2</sub> SiCH <sub>2</sub> SH <sup>+</sup> , 44/; 58, /(CH <sub>3</sub> ) <sub>2</sub> Si <sup>+</sup> , 50/
VII	356 (M <sup>+</sup> , 1%); 295, (M-SC <sub>2</sub> H <sub>5</sub> , 2); 267 (M-C <sub>2</sub> H <sub>5</sub> -SC <sub>2</sub> H <sub>5</sub> , 14); 234, /(CH <sub>3</sub> ) <sub>2</sub> SiC <sub>4</sub> H <sub>6</sub> (SC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> <sup>+</sup> , 10/; 221, /M-CH(SC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> , 2/; 207, /(C <sub>3</sub> ) <sub>2</sub> SiC <sub>2</sub> H <sub>3</sub> (SC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> , 100/
XI	264, M <sup>+</sup>
XII	241, M <sup>+</sup>
XIII	186 (M <sup>+</sup> , 50%); 157 (M-C <sub>2</sub> H <sub>5</sub> , 50); 131, /M-(C = CH)-CH <sub>2</sub> / <sup>+</sup> , 50/; 88, /CH <sub>2</sub> SiCH <sub>2</sub> CH <sub>2</sub> S <sup>+</sup> , 100/; 72, /SiCH <sub>3</sub> (C <sub>2</sub> H <sub>5</sub> ) <sup>+</sup> , 20/
XIV	186, (M <sup>+</sup> , 5%); 161, /M-(C≡CH), 14/; 146, (M-CH <sub>3</sub> -C <sub>2</sub> H <sub>5</sub> , 1); 132, /M-(C≡CH)-C <sub>2</sub> H <sub>5</sub> , 100/; 116, /SiC <sub>2</sub> H <sub>5</sub> (SCH <sub>2</sub> )CH <sup>+</sup> , 43/; 67, /SiCH <sub>2</sub> (C≡CH) <sup>+</sup> , 100/
XV	186, (M <sup>+</sup> , 1%); 159, /M-(C≡CH), 12/; 142, (M-CH <sub>3</sub> -C <sub>2</sub> H <sub>5</sub> , 3); 144, /M-(C≡CH <sub>2</sub> ), 67/; 125, (M-SC <sub>2</sub> H <sub>5</sub> , 2); 115, (SiCH = CHSC <sub>2</sub> H <sub>5</sub> <sup>+</sup> , 3); 101, (SiCH = CHSCH <sub>2</sub> <sup>+</sup> , 17); 97, / (CH <sub>3</sub> ) <sub>3</sub> Si(CH=CH <sub>2</sub> )CH-CH <sup>+</sup> , 67/; 69, (CH <sub>2</sub> SiCH = CH <sub>2</sub> <sup>+</sup> , 100)
XVI	248, (M <sup>+</sup> , 1%); 219, (M-C <sub>2</sub> H <sub>5</sub> , 1); 187, (M-SC <sub>2</sub> H <sub>5</sub> , 1); 161, (M-CH=CHSC <sub>2</sub> H <sub>5</sub> , 24); 129, (M-CH=CHSC <sub>2</sub> H <sub>5</sub> -S, 100) 41, (M-CH=CHSC <sub>2</sub> H <sub>5</sub> SC <sub>2</sub> H <sub>5</sub> , 100); 87, (CH=CHSC <sub>2</sub> H <sub>5</sub> <sup>+</sup> , 24).
XVII	310, (M <sup>+</sup> , 1%); 249, (M-SC <sub>2</sub> H <sub>5</sub> , 27); 221(M-C <sub>2</sub> H <sub>4</sub> SC <sub>2</sub> H <sub>5</sub> , 73); 219, /M-SC <sub>2</sub> H <sub>5</sub> -(CH <sub>3</sub> ) <sub>2</sub> , 5/; 192, (M-C <sub>2</sub> H <sub>4</sub> SC <sub>2</sub> H <sub>5</sub> -C <sub>2</sub> H <sub>5</sub> , 1); 160, (M-C <sub>2</sub> H <sub>4</sub> SC <sub>2</sub> H <sub>5</sub> -SC <sub>2</sub> H <sub>5</sub> , 27); 132, (CH <sub>3</sub> SiC <sub>2</sub> H <sub>4</sub> SC <sub>2</sub> H <sub>5</sub> <sup>+</sup> , 100); 105, /CH(SCH <sub>2</sub> ) <sub>2</sub> <sup>+</sup> , 77/
XVIII	(M <sup>+</sup> , 5%); 160, (M-CH=CHSC <sub>2</sub> H <sub>5</sub> , 48); 132, (CH <sub>3</sub> SiC <sub>2</sub> H <sub>4</sub> SC <sub>2</sub> H <sub>5</sub> <sup>+</sup> , 480); 105, /CH(SCH <sub>2</sub> ) <sub>2</sub> <sup>+</sup> , 31/; 77, (CHS <sub>2</sub> , 20)

trometer (thin layer). GLC-MS spectra were recorded on an MAT-212 mass spectrometer (70 Ev, gas-chromatograph Varian 2700, capillary column 20 m, SE-54 phase).

3.1. The photoinitiated addition of ethanethiol (**Ia**) and its derivatives (**Ib**, **c**, **d**) to diethynyl(dimethyl)silane (**II**) and diethynyl(methyl)ethylsilane (**III**) (general method)

A mixture of thiylation agents (**Ia**, **b**, **c**, **d**) with silane (**II**) or (**III**) is placed in a quartz vessel and irradiated with a DRT-400 UV-lamp from 2 to 16 h.

The reaction adducts are:



The adducts **V**, **XI**, **XII**, **XIII**, **XVII** and **XVIII** were isolated by vacuum distillation. Their physico-chemical constants and elemental analysis data are presented in Table 1. Their structure was confirmed by  $^1\text{H-NMR}$  (Table 2), IR spectroscopy (Table 3) and GLC-MS (Table 4).

The isomeric adducts **VI** and **VII** are isolated as a mixture in 52% yield and a **VI:VII** ratio of 1:2. The isomers **VI** and **VII** were identified in the mixture by  $^1\text{H-NMR}$  (Table 2) and GLC-MS (Table 4).

The isomeric adducts **IX** and **X** were also isolated as a mixture. The yield of this mixture is 14.6%, and the **IX:X** ratio is 3:7. The isomers **IX** and **X** were identified in the mixture by  $^1\text{H-NMR}$  (Table 2) and IR spectroscopy (Table 3).

The adducts **IV**, **XIV**, **XV** and **XVI** were identified in the reaction mixture by the help of  $^1\text{H-NMR}$ , IR spectroscopy and GLC-MS (Tables 2–4).

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