ISSN 1070-3632, Russian Journal of General Chemistry, 2008, Vol. 78, No. 9, pp. 1675–1681. © Pleiades Publishing, Ltd., 2008.
Original Russian Text © E.N. Suslova, A.I. Albanov, B.A. Shainyan, 2008, published in Zhurnal Obshchei Khimii, 2008, Vol. 78, No. 9, pp. 1442–1448.

Si-Disubstituted Diallylsilanes in Homolytic Thiylation and Electrophilic Fragmentation Reactions

E. N. Suslova, A. I. Albanov, and B. A. Shainyan

Favorskii Irkutsk Institute of Chemistry, Siberian Branch, Russian Academy of Sciences, ul. Favorskogo 1, Irkutsk, 664033 Russia
e-mail: bagrat@irioch.irk.ru

Received May 6, 2008

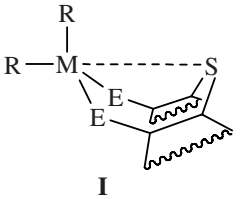
Abstract—Approaches to Si-disubstituted 1-thia-5-silacyclooctanes based on homolytic addition of hydrogen sulfide to diallylsilanes $R_2Si(CH_2CH{=}CH_2)_2$ and on intramolecular cyclization of Si-disubstituted (allyl)(γ-sulfanylpropyl)silanes have been studied. In the former case the reactivity of the silanes decreases in the order R = MeO > F > Me > Ph, whereas in the latter case the reactivity order is slightly different: Me > MeO ≈ F >> Ph. The reactions of diphenyl- and dimethyldiallylsilanes with the complex $BF_3{\cdot}2AcOH$ occur in a different manner: The former involves rearrangement to form fluoro(2-methylpent-4-enyl)diphenylsilane, while the latter, elimination of the two allyl groups to fluorodimethylsilane and propene.

DOI: 10.1134/S1070363208090065

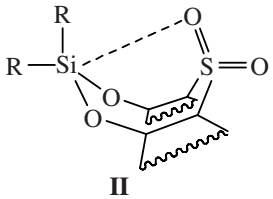
Diallylsilanes are of interest as precursors of eight-membered heterocycles, thiasilacyclooctanes and their sulfur oxidation products. The stereochemistry of heterocycles of this type is to a large extent determined by the presence of the two heteroatoms different in nature, relative position, and possibility to interact with each other. For example, in eight-membered cycles, such as trithia- and thia(dioxa)germacyclooctanes **I** [1], 1-thia-4,6-dioxa-5-silacyclooctane and its analogs **II** [2, 3], chelate cycles with intramolecular coordination S→Si(Ge) (**I**) or S=O→Si (**II**) bond stabilizing the *boat* conformation can form, as proved by X-ray diffraction analysis. Theoretical studies ([4] and references therein) showed that in Si-halogenated 1,4-silathiane *S*-oxides **III** (X, Y = F, Cl, Br), too, forma-tion of five-membered chelate cycles with the coordination S=O→Si bond is also possible.

In this connection it was of interest to investigate the possibility of preparation and the structure of thiasilacyclooctanes with electron-acceptor substituents at the silicon atom, in particular, 5,5-difluoro-1-thia-5-silacyclooctane $F_2Si[(CH_2)_3]_2S$ and its *S*-functional derivatives.

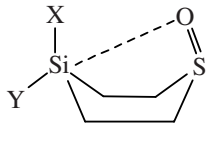
The syntheses of 5,5-dimethyl- and 5,5-diphenyl-1-thia-5-silacyclooctanes $R_2Si[(CH_2)_3]_2S$ by hydrogen sulfide addition to the corresponding diallylsilanes $R_2Si(CH_2CH{=}CH_2)_2$ at –78°C and UV irradiation (yield 10–25%) [5, 6] of 5,5-diethyl-1-thia-5-silacyclooctane by diethylsilane addition to diallyl sulfide followed by cyclization of the γ-adduct [7] have been reported. These and other syntheses of silicon-containing diheterocyclic compounds have been recently reviewed [8].



I



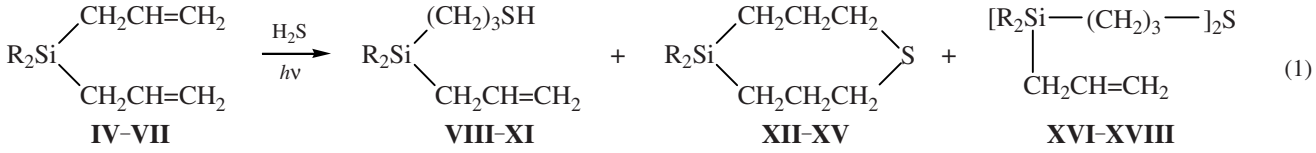
II



III

M = Si, Ge; E = O, S.

We earlier prepared 5,5-difluoro- and 5,5-dimethoxy-1-thia-5-silacyclooctanes $F_2Si[(CH_2)_3]_2S$ and $(MeO)_2Si[(CH_2)_3]_2S$ [9] and 5,5-dimethyl-1-thia-5-silacyclooctane $Me_2Si[(CH_2)_3]_2S$ [10] by homolytic thiylation of the corresponding diallylsilanes with gaseous H_2S (yield ~30%). We performed GC and NMR monitoring of this reaction with different diallylsilanes in cyclohexane and without a solvent. Apart from the starting silanes, we detected in the reaction mixture thiols and cyclic and linear sulfides.



IV–VII **VIII–XI** **XII–XV** **XVI–XVIII** (1)

R = F (**IV, VIII, XII, XVI**); MeO (**V, IX, XIII**); Ph (**VI, X, XIV, XVII**); Me (**VII, XI, XV, XVIII**).

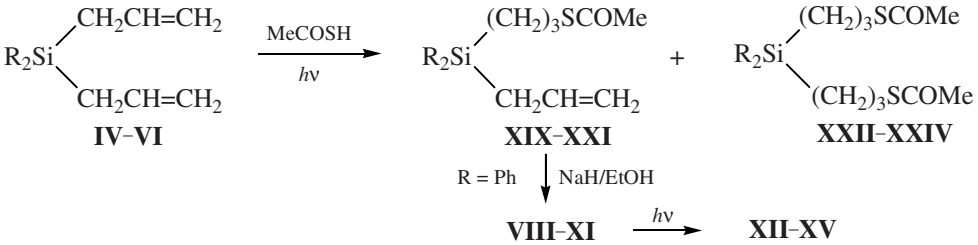
In the absence of solvent after 3 h at 50°C, the conversion of silanes **IV–VII** was 70–80% for R = F, MeO and ~40% (60% in 6 h) for R = Me. Diallyldiphenylsilane (**VI**) was found to be even less active: Its conversion was 20, 50, and 80% after 3, 7 and 13 h, respectively. The fraction of sulfides **XVI–XVIII** in the reaction products reached 20% (see also [10]).

Intramolecular cyclization of thiols **VIII–XI** proceeds regioselectively, in accordance with published data [5, 6, 10, 11]. The total content of thiols and thiasilacyclooctanes under these conditions is 52–55% (R = F, 3 h, **VIII**:**XII** = 1:1), 20% (R = Me, 3 h, **XI**:**XV** = 3:1), 32% (R = Me, 6 h, **XI**:**XV** = 2:1), 17% (R = Ph, 3 h, **X**:**XIV** = 100:0), 38% (R = Ph, 7 h, **X**:**XIV** = 9:1), and 60% (R = Ph, 13 h, **X**:**XIV** = 3:1). Further increase of the reaction time (R = Ph) leads only to an increase of the content of oligomerization products. The isolated products were thiol **X** in 32% yield and thiasilacyclooctane **XIV** in 11% yield.

With R = MeO, thiasilacyclooctane **XIII** was isolated in 23% yield; thiol (**IX**) could not be detected by GC. However, when the reaction was performed in cyclohexane for 3 h, 25% of thiol **IX** was formed at a 50% conversion. The reaction of diallyldifluorosilane (**IV**) in cyclohexane, too, gave more thiol **VIII** (**VIII**:**XII** 2:1), and it could be isolated pure. In the reaction of hydrogen sulfide with diallyldimethylsilane in cyclohexane, the conversion drops so drastically that only 8–10% of thiol **XI** and trace amounts of thiasilacyclooctane **XV** are formed. The yields of thiasilacyclooctanes **XII–XV** at various reaction conditions are given in Table 1.

Therefore, the reactivity of diallylsilanes **IV–VII** in the photochemical heterocyclization reaction (1) decreases in the order R = MeO > F > Me > Ph.

To increase the yield of thiasilacyclooctanes, we studied alternative synthetic approach involving intramolecular cyclization of independently synthesized thiols **VIII–X**. This approach was earlier suggested for thiol **XI** [5, 6, 12]. Thiols **VIII–X** were prepared by different methods to provide their highest yields. Thus thiol **X** was obtained in 60% yield by radical addition of thioacetic acid to diallyldiphenylsilane with subsequent saponification with sodium hydride in ethanol.



IV–VI **XIX–XXI** **XXII–XXIV** **VIII–XI** **XII–XV** (2)

R = Ph (**XIX, XXII**); F (**XX, XXIII**); MeO (**XXI, XXIV**).

Table 1. Reaction of diorganyldiallylsilanes $R_2Si(CH_2CH=CH_2)_2$ with hydrogen sulfide

R	Yield of thiasilacyclooctane	
	without solvent	in cyclohexane
F	28	16
MeO	30	24
Me	13 (25%, 6 h)	5
Ph	0 (11%, 13 h)	–

Table 2. Photochemical cyclization of thiols $R_2Si(CH_2CH=CH_2)(CH_2CH_2CH_2SH)$ into thiasilacyclooctanes $R_2Si(CH_2\cdot CH_2CH_2)_2S$

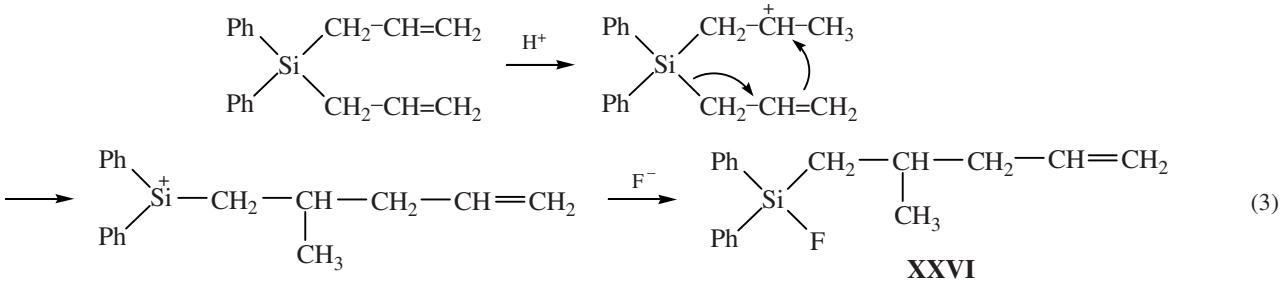
R	Yield of the cycle, %	
	after 1.5 h	after 3 h
F	16	24
MeO	10	23
Me	27	33
Ph	–	–

Mono- and dithioacetates **XIX** and **XXII** are easily separated by vacuum distillation. The intermediate mono- and dithioacetates were also prepared with diallyldifluoro- and diallyldimethoxysilanes, but their saponification was complicated by hydrolytic cleavage of the Si–F or Si–O bond. Therefore, thiol **VIII** was isolated by preparative GC from the reaction of silane **IV** with hydrogen sulfide, and thiols **IX** and **XI** were synthesized in 12 and 43% yields, respectively, by decomposition with dry ammonia of thiuronium salts prepared from the corresponding 3-chloropropylsilanes and thiourea (data of this work and ref. [11]).

The last step of reaction (2) (cyclization of thiols into thiasilacyclooctanes) was performed under UV irradiation of 5% solutions of thiols in cyclohexane at 55°C. From GC, the yields of thiacyclooctanes from thiols **VIII, IX**, and **XI** after 1.5 h were about 70% (per reacted thiol); however, because of strong tarring, the isolated yields of thiasilacyclooctanes **XII, XIII,** and **XV** were 18, 10 and 27%, respectively. Prolongation of the reaction time to 3–5 h allows to the yields to be increased 24–33%. Thiol **X** fails to cyclize under these conditions. Lowering the temperature to 0°C completely stops the reaction, while UV irradiation in the presence of benzoyl peroxide at 50°C leads, from ^1H and ^{29}Si NMR data, to formation of as little as 4–5% of heterocycle **XIV**.

The results of photochemical cyclization of organosilicon thiols into thiasilacyclooctanes are summarized in Table 2. As follows from these data, the reactivity order in this case is slightly different from that in reaction (1): Me > MeO ≈ F >> Ph.

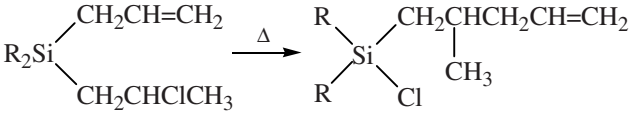
It follows from a comparison of the results of investigation of reactions (1) and (2) that the one-step reaction of diallylsilanes with hydrogen sulfide is the most suitable for preparing thiasilacyclooctanes with labile substituents at the silicon atom, in particular, with fluorine atoms. However, for this synthesis one needs hardly accessible diallyldifluorosilane. Therefore, taking into account the reported cleavage of the Si–Ph bond in the SiR_2Ph and $SiRPh_2$ groups by the action of the complexes $BF_3\cdot 2AcOH$ (**XXV**) and $HBF_4\cdot OEt_2$ to form compounds containing $SiFR_2$ and SiF_2R groups [13–15], we tried to convert diallyldiphenylsilane (**VI**) into diallyldifluorosilane (**IV**) in order to cyclize the latter into the target 5,5-difluoro-1-thia-5-silacyclooctane (**XII**). It should be noted that the allyl group in allyltrimethylsilanes $R_3SiCH_2CH=CHR$ is readily eliminated under the action of various electrophilic reagents, including fluorine-containing ones [16–18]. However, a priori it was difficult to predict the reaction pathway of complex **XXV** with diallyldiphenylsilane (**VI**) possessing two groups capable of elimination: allyl and phenyl. It turned out that neither silane **IV** nor its precursor, diallyl(fluoro)phenylsilane, nor any products of elimination of one or two allyl groups are formed; instead, we obtained a rearrangement product, fluoro(2-methylpent-4-enyl)diphenylsilane (**XXVI**) was obtained in 63% yield [19]. A mechanism of its formation was suggested, which involved the rearrangement of the carbocation with cleavage of the $Si–C_{sp3}$ bond by the $S_{E'}$ allylic substitution mechanism and addition of the fluoride ion to the resulting silyl cation [19].

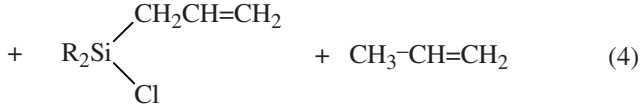


XXVI (3)

A direct analog of reaction (3) is the rearrangement of diorganyl(diallyl)silanes into diorganyl(fluoro)(2-methylpent-4-enyl)silanes $R_2Si(F)CH_2CH(Me)CH_2CH=CH_2$, that occurs as a side process in the reaction of the former with α,β-unsaturated ketones in the presence of $BF_3 \cdot OEt_2$. The yields of these products were 15, 0, and 5% for R = *i*-Pr, Pr and Ph, respectively [20].

A similar rearrangement, occurring in parallel with elimination of propene and formation of diorganyl (allyl)chlorosilanes, was observed during thermolysis of allyl(2-chloropropyl)dimethyl- and allyl(2-chloropropyl)diphenylsilanes [21].

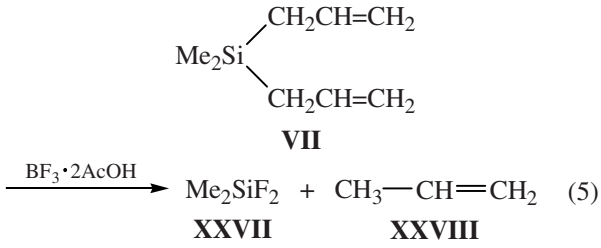




(4)

The product composition crucially depends on the substituent R: With for R = Me, the reaction by 95% proceeds as elimination of the allyl group, whereas with R = Ph, the rearrangement products predominates (70%) [21].

Taking into account such a strong effect of the substituent at silicon in allylsilanes on the product composition, we have studied the reaction of diallyldimethylsilane (**VII**) with the complex $BF_3 \cdot 2AcOH$. It was earlier shown that silane **VII** reacts with trifluoromethanesulfonic acid to form the product of elimination of one propene molecule, $Me_2Si(CH_2CH=CH_2)OSO_2CF_3$ [22]. It was found that with complex $BF_3 \cdot 2AcOH$, too, diallyldimethylsilane (**VII**) reacts differently than diallyldiphenylsilane (**VI**). Instead of the rearrangement product [see reaction (3)], only gaseous products of elimination of both allyl groups, difluorodimethylsilane (**XXVII**) and propene (**XXVIII**), formed and were trapped by bubbling into CCl_4 in a cooled trap.



VII

$$\xrightarrow{BF_3 \cdot 2AcOH} \underset{\textbf{XXVII}}{Me_2SiF_2} + \underset{\textbf{XXVIII}}{CH_3{-}CH{=}CH_2} \quad (5)$$

The formation of difluorodimethylsilane is unequivocally proved by the observation in the ^{19}F NMR spectrum of a septet coupling with $^3J_{HF}$ 6.1 Hz and a doublet of septets on ^{29}Si satellites with $^1J_{SiF}$ 290.7 Hz. Evidence for the formation of propene comes from the observation in the ^1H NMR spectrum of a doublet of the methyl group, two doublets of the $=CH_2$ group with characteristic J_{cis} and J_{trans} coupling constants, and a multiplet signal of the CH= proton (3:1:1:1), as well as the corresponding signals in the ^{13}C NMR spectrum.

Analysis of the pathway and mechanism of the reaction of diorganyldiallylsilanes with different acids as a function of the structure of the silane and the strength of the acid will be the subject of our further communication.

EXPERIMENTAL

The IR spectra were taken on a Specord IR-75 instrument in thin layer and in KBr. The NMR spectra were recorded on a Bruker DPX 400 spectrometer at 400 (^1H), 100 (^{13}C), 376 (^{19}F), 80 MHz (^{29}Si) for solutions in $CDCl_3$, references TMS (^1H, ^{13}C, ^{29}Si) and CCl_3F (^{19}F). The electron impact mass spectra (70 eV) were obtained on Shimadzu GCMS-QP5050A (compound **XII**) and Hewlett-Packard HP 5971A (compounds **XIV, XVII**) instruments.

Photochemical reactions were carried out in quartz flasks using a DRT-400 UV lamp. Column chromatography was performed on Silica 60 (Merck).

5,5-Diphenyl-1-thia-5-silacyclooctane (XIV). Dry hydrogen sulfide was bubbled through 6.93 g of diphenyldiallylsilane upon UV irradiation at 45–50°C. The reaction was followed by ^1H and ^{29}Si NMR spectroscopy by taking out samples every 2–3 h. After completion, the reaction mixture was repeatedly extracted with hexane and ether. After removal of the solvent from the extract, 1.3 g of starting silane **VI** and 1.98 g of thiol **X** was isolated by vacuum distillation. bp 180–186°C (1 mm Hg), yield 32% (per reacted silane). The residue insoluble in hexane and ether was the target 5,5-diphenyl-1-thia-5-silacyclooctane (**XIV**), yield 0.73 g (11% per reacted silane). An analytically pure sample was obtained by column chromatography on silica, eluents hexane, hexane–ether from 20:1 to 1:1, R_f 0.22, mp 73–74°C. IR spectrum, ν, cm^{-1}: 3060, 2900, 1580, 1410, 1100, 695. ^1H NMR spectrum, δ, ppm: 1.15 m (4H, $SiCH_2$), 1.55 m (4H, CH_2), 2.41 m (4H, CH_2S), 7.34–7.48 m (10H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 12.23 ($SiCH_2$), 24.01 (CH_2), 35.71

(CH_2S), 127.97 (C_m), 129.40 (C_p), 134.94 (C_o), 135.63 (C^1). ^{29}Si NMR spectrum, δ_{Si}, ppm: –6.64. Mass spectrum, *m/z*, (I_{rel}, %, ion): 298 (0.1, $[M]^{+\cdot}$), 256 (5.6, $[M - C_3H_6]^{+\cdot}$), 221 (100, $[M - Ph]^+$), 179 (49, $[221 - C_3H_6]^+$), 137 (13, $[179 - C_3H_6]^+$). The fragmentation of the molecular ion is similar to that described for 5,5-dimethyl-1-thia-5-silacyclo-octane [5]. Found, %: C 72.78; H 7.46; S 9.87; Si 9.57. $C_{18}H_{22}SSi$. Calculated, %: C 72.48; H 7.38; S 10.74; Si 9.40.

Cyclization of diorganyldiallylsilanes **IV, V**, and **VII** was performed in a similar way.

5,5-Difluoro-1-thia-5-silacyclooctane (XII). ^1H NMR spectrum, δ, ppm: 0.89 m (4H, $SiCH_2$), 1.85 m (4H, CH_2), 2.54 m (4H, CH_2S). ^{13}C NMR spectrum, δ_C, ppm: 12.09 t ($SiCH_2$, *J* 15.7 Hz), 23.09 (CH_2), 33.32 (CH_2S). ^{19}F NMR spectrum, δ, ppm: –131.11 d (*J* 294 Hz). ^{29}Si NMR spectrum, δ_{Si}, ppm: –3.08 t (*J* 291 Hz). Mass spectrum, *m/z*, (I_{rel}, %, ion): 182 (31, $[M]^{+\cdot}$), 140 (100, $[M - C_3H_6]^{+\cdot}$), 139 (72, $[140 - H]^+$), 106 (24, $[140 - H_2S]^{+\cdot}$).

5,5-Dimethoxy-1-thia-5-silacyclooctane (XIII). ^1H NMR spectrum, δ, ppm: 0.79 m (4H, $SiCH_2$), 1.82 m (4H, CH_2), 2.52 m (4H, CH_2S), 3.51 s (6H, MeO) (coincides with published data [9]). ^{13}C NMR spectrum, δ_C, ppm: 10.39 ($SiCH_2$), 23.47 (CH_2), 34.09 (CH_2S), 50.27 (MeO). ^{29}Si NMR spectrum, δ_{Si}, ppm: –2.21.

Bis[3-(allyldifluorosilyl)propyl] sulfide (XVI). ^1H NMR spectrum, δ, ppm: 0.95 m (4H, $SiCH_2$), 1.74 m (4H, CH_2), 1.88 m (4H, $SiCH_2Vi$) 2.53 t (4H, CH_2S, *J* 6.85 Hz), 5.05 d (1H, $=CH^A$, *J* 9.7 Hz), 5.09 d (1H, $=CH^B$, *J* 17.4 Hz), 5.76 d.d.t (2H, CH=, *J* 8.0, 9.7, 17.4 Hz). ^{13}C NMR spectrum, δ_C, ppm: 11.13 t ($SiCH_2$, *J* 14.57 Hz), 19.79 t ($SiCH_2Vi$, *J* 14.19 Hz), 21.65 (CH_2), 34.55 (CH_2S), 117.25 ($=CH_2$), 129.12 (=CH). ^{19}F NMR spectrum, δ_F, ppm: –139.64 q, (*J* 306.2, 5.0 Hz). ^{29}Si NMR spectrum, δ_{Si}, ppm: –5.03 t (*J* 306.2 Hz).

Bis[3-(allyldiphenylsilyl)propyl] sulfide (XVII). ^1H NMR spectrum, δ, ppm: 0.89 m (4H, $SiCH_2$), 1.65 m (4H, CH_2), 2.12 d (4H, $SiCH_2Vi$, *J* 7.9 Hz), 2.53 m (4H, CH_2S), 4.93 m (4H, $=CH_2$), 5.81 d. d. t (2H, CH=, *J* 8.5, 9.3, 17.2 Hz). ^{29}Si NMR spectrum, δ_{Si}, ppm: –15.03. Mass spectrum, *m/z*, (I_{rel}, %, ion): 521 (56, $[M - C_3H_5]^+$), 223 (100, $[Ph_2SiCH_2CH{=}CH_2]^+$), 183 (29, $[223 - C_3H_4]^+$).

Reaction of disubstituted diallylsilanes with thioacetic acid. To 5.15 g of diallyldiphenylsilane in 10 ml of cyclohexane, 1.2 g of thioacetic acid in 2 ml of cyclohexane was added dropwise at 50°C over the course of 1 h, and the mixture was refluxed for 5.5 h. After removal of the solvent and vacuum distillation, 2.52 g of monothioacetate **XIX** was isolated with bp 185–187°C (1 mm Hg), yield 56% (per reacted silane), and 1.21 g of dithioacetate **XXII**, bp 200–202°C (1 mm Hg), yield 28%. Analytically pure samples were obtained by column chromatography on silica, eluents hexane, hexane–ether, 15:1–5:1.

The reactions of difluorodiallylsilane and dimethoxy–diallylsilane with thioacetic acid and separation of the products was carried out in a similar way, except that the reaction mixtures were additionally UV irradiated.

Allyldiphenyl[3-(thioacetoxy)propyl]silane (XIX). R_f 0.3. IR spectrum, ν, cm^{-1}: 3050, 2910, 1690, 1620. 1590, 1410, 1120–1100, 690. ^1H NMR spectrum, δ, ppm: 1.21 m (2H, $SiCH_2$), 1.68 m (2H, CH_2), 2.15 m (2H, $SiCH_2Vi$), 2.33 s (3H, CH_3), 2.92 m (2H, CH_2S), 4.92 m (2H, $=CH_2$), 5.79 m (1H, CH=), 7.39–7.51 m (10H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 11.87 ($SiCH_2$), 20.47 ($SiCH_2Vi$), 24.06 (CH_2), 30.70 (CH_2S), 114.64 ($=CH_2$), 127.97 (C_m), 129.51 (C_o), 133.80 (=CH), 134.95 (C_p), 135.21 (C^1), 195.80 (C=O). ^{29}Si NMR spectrum, δ_{Si}, ppm: –9.38. Found, %: C 70.73; H 6.97; S 9.17; Si 7.97. $C_{20}H_{24}OSSi$. Calculated, %: C 70.55; H 7.10; S 9.41; Si 8.24.

Diphenylbis[3-(thioacetoxy)propyl]silane (XXII). R_f 0.1. IR spectrum, ν, cm^{-1}: 3040, 2915, 1690, 1590, 1410, 1115–1100, 695. ^1H NMR spectrum, δ, ppm: 1.17 m (4H, $SiCH_2$), 1.63 m (4H, CH_2), 2.33 s (6H, CH_3), 2.90 m (4H, CH_2S), 7.36–7.48 m (10H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 12.16 ($SiCH_2$), 24.14 (CH_2), 30.68 (CH_3), 32.56 (CH_2S), 127.98 (C_m), 129.46 (C_o), 134.84 (C_p), 135.19 (C^1), 195.76 (C=O). ^{29}Si NMR spectrum, δ_{Si}, ppm: –6.96. Found, %: C 62.86; H 6.68; S 14.20; Si 7.00. $C_{22}H_{28}O_2S_2Si$. Calculated, %: C 63.42; H 6.77; S 15.39; Si 6.73.

Allyldifluoro[3-(thioacetoxy)propyl]silane (XX). Yield 30%, bp 90–95°C (6 mm Hg). ^1H NMR spectrum, δ, ppm: 0.76 m (2H, $SiCH_2$), 1.62 m (2H, CH_2), 1.79 m (2H, $SiCH_2Vi$), 2.31 s (3H, CH_3), 2.86 t (2H, CH_2S, *J* 7.12 Hz), 5.02 d (1H, $=CH^A$, *J* 9.8 Hz), 5.05 d (1H, $=CH^B$, *J* 17.2 Hz), 5.71 d. d. t (1H, CH=, *J* 7.5, 9.7, 17.4 Hz). ^{13}C NMR spectrum, δ_C, ppm: 11.04 t ($SiCH_2$, *J* 15.11 Hz), 19.49 ($SiCH_2Vi$), 22.34 (CH_2), 30.50 (CH_3), 31.66 (CH_2S), 117.16 ($=CH_2$), 128.85 (=CH), 195.85 (C=O). ^{19}F NMR spectrum, δ_F, ppm:

–139.61 quintet, (J ~302, 7.5 Hz). ^{29}Si NMR spectrum, δ_{Si}, ppm: –0.13 t (J ~302 Hz).

Difluorobis[3-(thioacetoxy)propyl]silane (XXIII). Yield 25%, bp 140–145°C (6 mm Hg). ^{1}H NMR spectrum, δ, ppm: 0.85 m (4H, $SiCH_2$), 1.69 m (4H, CH_2), 2.31 s (6H, CH_3), 2.86 t (4H, CH_2S, J 6.98 Hz). ^{13}C NMR spectrum, δ_C, ppm: 11.58 t ($SiCH_2$, J 14.4 Hz), 21.77 (CH_2), 30.50 (CH_3), 31.39 (CH_2S), 195.36 (C=O). ^{19}F NMR spectrum, δ_F, ppm: –139.22 quintet (J 304.2, 7.53 Hz).^{29}Si NMR spectrum, δ_{Si}, ppm: –0.14 t (J 304.2 Hz).

Allyldimethoxy[3-(thioacetoxy)propyl]silane (XXI). Yield 40%, bp 155–160°C (6 mm Hg), n_D^{19} 1.4720. ^{1}H NMR spectrum, δ, ppm: 0.68 m (2H, $SiCH_2$), 1.57 m (2H, CH_2), 1.61 d (2H, $SiCH_2Vi$, J 7.7 Hz), 2.26 s (3H, CH_3), 2.82 t (2H, CH_2S, J 7.1 Hz), 3.48 s (6H, MeO), 4.89 d (1H, $=CH^A$, J 10.0 Hz), 4.92 d (1H, $=CH^B$, J 17.0 Hz), 5.74 d. d. t (1H, CH=, J 8.2, 10.0, 17.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 11.13 ($SiCH_2$), 19.74 ($SiCH_2Vi$), 23.03 (CH_2), 30.53 (CH_3), 32.08 (CH_2S), 50.46 (CH_3O), 114.71 ($=CH_2$), 132.58 (=CH), 195.55 (C=O). ^{29}Si NMR spectrum, δ_{Si}, ppm: –9.7.

Dimethoxybis[3-(thioacetoxy)propyl]dimethoxysilane (XXIV). Yield 23%, bp 215–220°C (6 mm Hg), n_D^{19} 1.4961. ^{1}H NMR spectrum, δ, ppm: 0.63 m (4H, $SiCH_2$), 1.57 m (4H, CH_2), 2.25 s (3H, CH_3), 2.81 t (4H, CH_2S, J 7.5 Hz), 3.44 s (6H, MeO). ^{13}C NMR spectrum, δ_C, ppm: 11.39 ($SiCH_2$), 23.15 (CH_2), 30.57 (CH_3), 32.09 (CH_2S), 50.30 (MeO), 195.42 (C=O). ^{29}Si NMR spectrum, δ_{Si}, ppm: –5.49.

Allyldiphenyl(3-sulfanylpropyl)silane (X). To a solution of sodium hydride in 13 ml of ethanol (pH 9–10), 2 g of allyldiphenyl[3-(thioacetoxy)propyl]silane in 11 ml of ethanol was added dropwise over the course of 1 h under argon, and the mixture was refluxed for 6 h. After filtration and removal of the solvent in the presence of the (4-*tert*-butylcatechol) inhibitor, 1.08 g (62%) of thiol **X** was isolated by vacuum distillation, bp 160–165°C (1 mm Hg). An analytically pure sample was obtained by column chromatography on silica, eluent hexane–ether, 80:1–15:1. R_f 0.61. IR spectrum, ν, cm^{-1}: 3060, 2905, 2560, 1620, 1580, 1405, 1095, 680. ^{1}H NMR spectrum, δ, ppm: 1.23 m (2H, $SiCH_2$), 1.33 t (1H, SH, J 8.1 Hz), 1.72 m (2H, CH_2), 2.14 d (2H, $SiCH_2Vi$, J 7.9), 2.55 m (2H, CH_2S), 4.92 m (2H, $=CH_2$), 5.80 m (1H, CH=), 7.39–7.52 m (10H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 11.45 ($SiCH_2$), 20.52 ($SiCH_2Vi$), 28.20 (CH_2), 28.46 (CH_2S), 114.61 ($=CH_2$), 127.83 (C_m), 129.49 (C_p), 133.83 (=CH), 135.03 (C_o), 135.06 (C^1). ^{29}Si NMR spectrum, δ_{Si}, ppm: –9.23. Found, %: C 72.27; H 7.27; S10.34; Si 9.83. $C_{18}H_{22}SSi$. Calculated, %: C 72.48; H 7.38; S 10.73; Si 9.39.

The NMR spectra of compounds **VIII** and **XI** coincide with those reported in [9, 12].

Allyldimethoxy(3-sulfanylpropyl)allylsilane (IX). A mixture of 6.3 g of ıallyl(3-chloropropyl)dimethoxysilane, 2.29 g of thiourea, and 0.063 g of tetrabutylammonium iodide in 5 ml of DMF was heated at 90°C over the course of 20 h, decomposed with dry ammonia for 1.5 h, diluted with 15 ml of pentane, and argon was bubbled with stirring for 45 min. The precipitate was extracted with methanol and filtered off. After removal of the solvent and vacuum distillation, 0.78 g (13%) of thiol **IX** was obtained, bp 83–85°C (10 mm Hg), n_D^{20} 1.4633. IR spectrum, ν, cm^{-1}: 2915, 2560, 1630, 1395, 1055, 800.

Photochemical cyclization of thiols was performed as described in [12].

Reaction of dimethyldiallylsilane with complex BF_3·2AcOH. To 0.815 g of diallyldimethylsilane in 50 ml of CH_2Cl_2, a solution of 1.09 g of BF_3·2AcOH in 20 ml of CH_2Cl_2 was added dropwise over the course of 1.5 h under argon at room temperature; the temperature increased to 32°C. The evolved gaseous products were trapped in a bubbler with CCl_4, cooled to –20°C. After completion, the reaction mixture was stirred for 30 min at room temperature and refluxed until gas evolution ceased (~30 min). The solution of the evolved gaseous products in CCl_4, contained a mixture of difluorodimethyl-silane and propene (NMR data, internal reference cyclohexane).

Difluorodimethylsilane (XXVII). ^{1}H NMR spectrum, δ, ppm: 0.27 t (CH_3, J 1.2 Hz). ^{19}F, δ_F, ppm: –129.79 septet ($^1J_{SiF}$ 290.7, $^3J_{HF}$ 6.1 Hz).

Propene (XXVIII). ^{1}H NMR spectrum, δ, ppm: 1.66 d (3H, CH_3, J 6.4 Hz), 4.83 d (1H, $=CH_{cis}$, J 10.1 Hz), 4.91 d (1H, $=CH_{trans}$, J 17.0 Hz), 5.69 d.d.q (1H, CH=, J 17.0, 10.1, 6.4 Hz). ^{13}C NMR spectrum, δ_C, ppm: 18.81 (CH_3), 115.39 ($=CH_2$), 132.48 (CH=).

ACKNOWLEDGMENTS

The authors are grateful to Yu.A. Chuvashev for taking the mass spectra and S.V. Kirpichenko (Irkutsk Institute of Chemistry) for helpful discussion of the results.

REFERENCES

1. Gonzalez-Montiel, S., Andrade-Lopez, N., Garcia-Montalvo, V., Cogordan, J.A., and Alvarado-Rodriguez, J.G., *Eur. J. Inorg. Chem*., 2006, no. 23, p. 4752.
2. Prakasha, T.K., Srinivasan, S., Chandrasekaran, A., Day, R.O., and Holmes, R.R., *J. Am. Chem. Soc*., 1995, vol. 117, no. 40, p. 10003.
3 Chandrasekaran, A., Day, R.O., and Holmes, R.R., *Organometallics,* 1996, vol. 15, no. 14, p. 3189.
4. Shainyan, B.A., *Int. J. Quant. Chem.*, 2007, vol. 107, no. 1, p. 189.
5. Koenig, K.E. and Weber, W.P., *Tetrahedron Lett*., 1973, vol. 14, no. 34, p. 3151.
6. Koenig, K.E., Felix, R.A., and Weber, W.P., *J. Org. Chem*., 1974, vol. 39, no. 11, p. 1539.
7. Voronkov, M.G., Kirpichenko, S.V., Keiko, V.V., and Tseitlina, E.O., *Izv. Akad. Nauk SSSR. Ser. Khim.*, 1981, no. 1, p. 174.
8. Rousseau, G. and Blanco, L., *Tetrahedron*, 2006, vol. 62, no. 34, p. 7951.
9. Voronkov, M.G., Kirpichenko, S.V., Suslova, E.N., Abrosimova, A.T., Keiko, V.V., and Albanov, A.I., *Zh. Obshch. Khim.,* 1983, vol. 53, no. 10, p. 2403.
10. Voronkov, M.G., Vlasova, N.N., Adamovich, M.Yu., Rakhlin, V.I., and Vitkovskii, V.Yu., *Zh. Obshch. Khim*., 1984, vol. 54, no. 7, p. 1566.
11. Kirhichenko, S.V., Tolstikova, L.L., Suslova, E.N., Albanov, A.I., and Voronkov, M.G., *Phosphorus, Sulfur Silicon*, 1995, vol. 106, no. 1, p. 47.
12. Voronkov, M.G., Kirpichenko, S.V., Suslova, E.N., Keiko, V.V., and Albanov, A.I., *Zh. Obshch. Khim.,* 1983, vol. 53, no. 10, p. 2404.
13. Fleming, I. and Kilburn, J.D., *J. Chem. Soc., Perkin Trans. 1*, 1998, no. 17, p. 2663.
14. Knolker, H.-J., Baum, G., Schmitt, O., and Wanzl G., *Chem. Commun.*, 1999, no. 17, p. 1737.
15. Akiyama, T., Hoshu, E., and Fujiyoshi, S., *J. Chem. Soc., Perkin Trans. 1*, 1998, no. 14, p. 2121.
16. Morita, T., Okamoto, Y., and Sakurai, H., *Synthesis*, 1981, no. 9, p. 745.
17. Hosomi, A., Ando, M., and Sakurai, H., *Chem. Lett*., 1981, no. 8, p. 1385.
18. Olah, G.A. and Rochin, C., *J. Org. Chem*., 1987, vol. 52, no. 4, p. 701.
19. Suslova, E.N., Albanov, A.I., and Shainyan, B.A., *Russ. J. Gen. Chem.*, 2008, vol. 78, no. 5, p. 1016.
20. Akiyama, T., Asayama, K., and Fujiyoshi, S., *J. Chem. Soc., Perkin Trans. 1*, 1998, no. 22, p. 3655.
21. Manuel, G., Bertrand, G., Mazerolles, P., and Ancelle, J., *J. Organomet. Chem.*, 1981, vol. 212, no. 3, p. 311.
22. Uhlig, W., *J. Organomet. Chem*., 1993, vol. 452, nos. 1–2, p. 29.