HYDROSILYLATION OF DIALKENYL SULPHIDES

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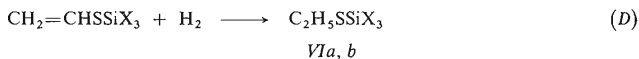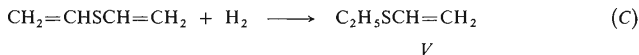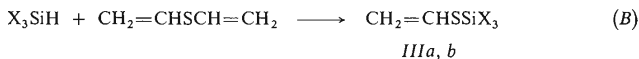*Siberian Division of the Academy of Sciences of the U.S.S.R., 664033 Irkutsk, USSR*
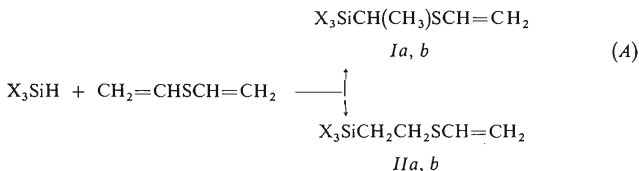
Hydrosilylation of divinyl and diallyl sulphide by triethyl- and triethoxysilane catalysed by $H_2PtCl_6.6 H_2O$ and $[RhCl\{P(C_6H_5)_3\}_3]$ has been studied. With divinyl sulphide the addition of X_3SiH ($X = C_2H_5$ or OC_2H_5) across the double bond proceeded to a negligible extent, the main reaction route being the cleavage of the $=CH-S$ bond. The course of the reaction of diallyl sulphide depended strongly upon the catalyst and the starting silicon hydride. In the presence of both catalysts triethoxysilane adds to diallyl sulphide to form a mixture of both isomeric monoadducts (β and γ) in relative amounts depending upon the catalyst. Contrary to this, the γ-adduct is formed solely in the chloroplatinic acid catalysed hydrosilylation of the above compound by triethylsilane whereas the cleavage of the C—S bond is predominant reaction in the presence of the rhodium catalyst. Some further side reactions are also reported.

The reaction of dialkenyl sulphides of the type $CH_2=CHS(CH_2)_nCH=CH_2$ ($n = 1, 2$) with $HSiR_nX_{3-n}$ has been reported to proceed in the presence of a platinum catalyst in accordance to Farmer's rule, involving the C=C bond more remote rom the sulphur atom[1]. However, divinyl sulphide reacts with diethylsilane to give a mixture of α- and β-silylsubstituted adducts with the former as prevailing product[2]. The addition of dialkylfluorosilanes to divinyl and diallyl sulphides yields isomeric monoadducts in high yields[3].

We now report on the reaction of triethyl- and triethoxysilane with divinyl and diallyl sulphides catalysed by H_2PtCl_6 and $[RhCl\{P(C_6H_5)_3\}_3]$. Contrary to reported data[1-3] both organosilicon hydrides employed in the study add to divinyl sulphide in the presence of chloroplatinic acid to a negligible extent. The reaction of triethylsilane leads to isomeric adducts *Ia* and *IIa* (equation (A), $X = C_2H_5$) in 6·2 and 6·9% yield, respectively. With triethoxysilane (Eq. (A), $X = C_2H_5O$) the total yield of adducts *Ib* and *IIb* is even smaller (see Experimental). In this case the β--adduct is prevailing (the *Ib* : *IIb* mol. ratio = 2 : 1).

With both silicon hydrides the predominant route is the cleavage of the $=CH—S$ bond of the sulphide to give the corresponding vinylthiosilane (compounds *IIIa* and *IIIb*, Eq. (*B*)), which in the case of triethylsilane is obtained in 22·5% yield. The C—S bond cleavage leads also to formation of hexaethyldisilthiane, $(C_2H_5)_3SiSSi(C_2H_5)_3$ (*IVa*) in 2·2% yield.

$$X_3SiCH(CH_3)SCH=CH_2$$
$$Ia, b$$

$$X_3SiH + CH_2=CHSCH=CH_2 \quad \xrightarrow{\quad\quad} \quad (A)$$

$$X_3SiCH_2CH_2SCH=CH_2$$
$$IIa, b$$

$$X_3SiH + CH_2=CHSCH=CH_2 \longrightarrow CH_2=CHSSiX_3 \quad (B)$$
$$IIIa, b$$

$$CH_2=CHSCH=CH_2 + H_2 \longrightarrow C_2H_5SCH=CH_2 \quad (C)$$
$$V$$

$$CH_2=CHSSiX_3 + H_2 \longrightarrow C_2H_5SSiX_3 \quad (D)$$
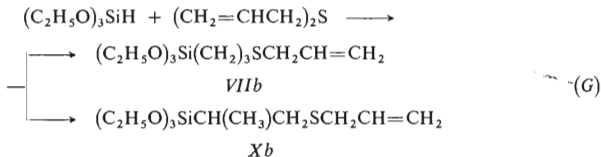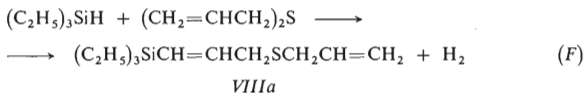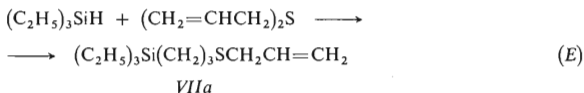$$VIa, b$$

In the presence of H_2PtCl_6 the hydrosilylation of divinyl sulphide is accompanied by other side reactions; polymerisation of the sulphide and hydrogenation of both the starting sulphide (Eq. (*C*), 1% yield, by g.l.c.) and the cleavage products (Eq. (*D*), *VIa*, 5·4% yield). The latter reaction has been reported to occur also during hydrosilylation of other unsaturated compounds[45].

Which one of the above reactions prevails is dependent upon the "age" of the catalyst. The freshly prepared catalyst, containing mainly a Pt(IV) species, induces polymerization. The resulting polymers are similar in their properties to those produced by polymerization of divinyl sulphide by Lewis acids[6]. By contrast to it, all the above processes, including hydrosilylation, take place with the catalyst set aside for more than 4 months which contains mainly a platinum(II) species. The use of the rhodium catalyst, $[RhCl\{P(C_6H_5)_3\}_3]$, does not result in an enhanced selectivity of this hydrosilylation, although with triethoxysilane the β-adduct (*IIb*) is formed in much greater relative amounts compared to the chloroplatinic acid catalysed addition (the β/α isomer ratio is 14 : 1 compared to 3 : 1 in the latter case). Moreover, the reaction of triethylsilane with the sulphide proceeds under milder conditions (100°C, 8 h) under which chloroplatinic acid is inactive. The yields of isomeric adducts *Ia*

and *IIa* are, however, very low $(2 \cdot 1\%$ each$)$. The main product is that of the $=$CH—S bond cleavage, CH_2=$CHSSi(C_2H_5)_3$ *(IIIa*, 22·9% yield), similarly to the reaction catalysed by H_2PtCl_6. Analogous product *(IIIb)* is obtained also with triethoxysilane. Formation of the product *VIb* indicates that also in this case hydrogenation is a detectable side reaction.

In contrast to divinyl sulphide, diallyl sulphide reacts with triethylsilane in the presence of chloroplatinic acid to form γ-adduct *VIIa* (Eq. *(E)*) in 60—70% yield under fairly mild conditions. Hydrosilylation occurs exclusively according to Farmer's rule, the C—S bond cleavage being negligible, as indicated by trace amounts of $(C_2H_5)_3$ . . $SiSCH_2CH$=CH_2 *(VIIIa*, 2—4% yield$)$.

$$(C_2H_5)_3SiH \ + \ (CH_2{=}CHCH_2)_2S \ \longrightarrow$$
$$\longrightarrow \ (C_2H_5)_3Si(CH_2)_3SCH_2CH{=}CH_2 \qquad\qquad (E)$$
$$VIIa$$

$$(C_2H_5)_3SiH \ + \ (CH_2{=}CHCH_2)_2S \ \longrightarrow$$
$$\longrightarrow \ (C_2H_5)_3SiCH{=}CHCH_2SCH_2CH{=}CH_2 \ + \ H_2 \qquad (F)$$
$$VIIIa$$

$$(C_2H_5O)_3SiH \ + \ (CH_2{=}CHCH_2)_2S \ \longrightarrow$$
$$\left[\begin{array}{l} \longrightarrow \ (C_2H_5O)_3Si(CH_2)_3SCH_2CH{=}CH_2 \\ \qquad\qquad VIIb \\ \longrightarrow \ (C_2H_5O)_3SiCH(CH_3)CH_2SCH_2CH{=}CH_2 \\ \qquad\qquad Xb \end{array}\right. \qquad (G)$$

The addition catalysed by $[RhCl\{P(C_6H_5)_3\}_3]$ proceeds similarly. In this case, however, the γ-adduct *VIIa* is formed in much lower yield. The predominant reaction is the C—S bond cleavage to give the corresponding derivative *VIIIa* in about 40% yield. This cleavage takes place under relatively mild conditions. Thus, after heating an equimolar mixture of triethylsilane and diallyl sulphide at 100°C for 2 h the reaction mixture contained 10% of *VIIIa*. The yield of this compound increases with increasing temperature and reaction time. The reaction leads also to the unexpected product $(C_2H_5)_3SiCH$=$CHCH_2$—SCH_2CH=CH_2 *(IXa)*, which is produced by dehydrocondensation reaction (Eq. *(F)*). The occurrence of such a reaction during hydrosilylation of some other unsaturated compounds has been reported also by other authors[7]. A somewhat different situation has been found in the diallyl sulphide + triethoxysilane reaction. With both catalysts only two isomeric adducts

(*VIIb* and *Xb*) are formed (Eq. (*G*)), the molar ratio of which depends upon the catalyst. Comparison of the β : γ isomer ratio for chloroplatinic acid (1 : 2) and the rhodium complex (1 : 20) shows that the latter compound is more selective catalyst. The use of benzene as a solvent in the rhodium-catalysed reaction decreases yields of the adducts without affecting the course of the reaction. It should be mentioned further that $[RhCl\{P(C_6H_5)_3\}_3]$ catalyses disproportionation of triethoxysilane to tetraethoxysilane. This by-product forms in hydrosilylation of both sulphides studied.

Summarizing, the reaction of both silicon hydrides with studied alkenyl sulphides follows two main routes. These are the addition of Si—H bond across the double C—C bond and the cleavage of the C—S bond of the sulphides (the latter one is also catalytic in nature; no reaction takes place between the silicon hydrides and the alkenyl sulphides on prolonged heating (100—150°C) in the absence of the catalysts). The relative importance of these processes depends upon the structure of the reactants and on the type of the catalyst.

EXPERIMENTAL

Compounds used. Chloroplatinic acid(hexahydrate), Kovohutě Vestec, was commercial sample. $[RhCl\{P(C_6H_5)_3\}_3]$ was prepared by reported procedure[11]. Diallyl sulphide was prepared from allyl bromide and sodium sulphide in the usual way[12]. Divinyl sulphide was freshly distilled before use.

Procedure. A glass ampoule was charged under argon with a sulphide, a silicon hydride and an isopropanol solution of $H_2PtCl_6.6\ H_2O$. In the case of the $[RhCl\{P(C_6H_5)_3\}_3]$ — catalysed reaction, the catalyst was weighed first and then the reactants were introduced in the above sequence. Sealed ampoules were heated to reaction temperature which was kept constant within $\pm0.5°C$. During the reaction the contents were vibrationally mixed. Experimental conditions are given in Tables I—III.

Chromatographic analysis. The reaction mixtures obtained in the above described way were subjected to gas chromatographic analysis. This was performed on a Chrom III instrument equipped with a thermal conductivity detector (2·4 m × 4 mm column packed with 5% XE 60 Silicone on Chesasorb (45—60 mesh), using programmed temperature (4°C/min from 80°C). Yields were determined by the internal standard method (Tables I and III).

Separation of products. The products were isolated by preparative gas chromatography using the same instrument as above which was equipped with a column (3·0 m × 10 mm) packed with 10% Lukopren G-1000 on Chromaton AW-HMDS for triethoxysilyl derivatives and with 15% Carbowax 20 M on the same support for triethylsilyl derivatives.

Structure determination. Hydrosilylation, cleavage and hydrogenation products isolated from reactions of divinyl and diallyl sulphide with triethyl- and triethoxysilane are summarized in Table IV. Elemental analyses performed for compounds *Ia*, *IVa*, *VIIa*, *VIIIa* and *Xa* agreed well with calculated data. IR spectra were recorded on a Zeiss Model UR 20 spectrophotometer in the 4000—400 cm^{-1} region *in substantia* (thin films). The spectra of compounds *Ib*—*IIIb* showed $\nu(SCH{=}CH_2)$ absorption bands at 1580—1582 cm^{-1}. NMR spectra were recorded on a Tesla Model BS 487 C spectrometer operating at 80 MHz (10% solutions of the compounds in CCl_4). Chemical shifts are given in δ (tetramethylsilane as internal reference).

TABLE I

Experimental Conditions for Reaction of Divinyl Sulphide with Triethyl- and Triethoxysilane
For procedure see Experimental.

Silicon hydride mol . 10^3	Sulphide mol . 10^3	$H_2PtCl_6^a$ mol . 10^6	$[RhCl\{P(C_6H_5)_3\}_3]$ mol . 10^6	h/°C
		$(CH_2{=}CH)_2S + (C_2H_5)_3SiH^{b,c}$		
30	30	5	—	24/150
4·77	4·77	—	5·2	8/100
		$(CH_2{=}CH)_2S + (C_2H_5O)_3SiH^d$		
50	50	10	—	46/150—160
50	50	—	1·1, 6	46/100—120

[a] Hexahydrate; 0·1M isopropanol solution. [b] Fractional distillation of the reaction mixture obtained by the chloroplatinic catalysed reaction afforded a fraction boiling at 32—100°C/0·53 kPa. This contained 10·9% of *Ia*, 11·9% of *IIa*, 33·6% of *IIIa*, 4·9% of *IVa*, 8·2% of *VIa* and 8·5% of hexaethyldisiloxane. [c] The mixture obtained by the rhodium complex–catalysed reaction contained 12·3% of the starting sulphide, 84·1% of the silicon hydride, 2·1% of *Ia*, 2·1% of *IIa* and 19·8% of *IIIa*. [d] Conversion of both divinyl sulphide and triethoxysilane did not exceed 15%. Composition of the two fractions obtained is presented in Table II.

TABLE II

Composition of Fractions 1 and 2 Obtained by Reaction of Divinyl Sulphide with Triethoxysilane

Catalyst	Fraction 1	Fraction 2[a]
$H_2PtCl_6.6\,H_2O$	45—120°C/0·13 kPa, $(C_2H_5O)_3Si_2O, V^b$, CH_3COCH_3	120°C/0·13 kPa, *Ib* : *IIb* : *IIIb* : *IVb* = = 3 : 5 : 3 : 8
$[RhCl\{P(C_6H_5)_3\}_3]$	70—145°/13·3 kPa, $(C_2H_5O)_4Si^b$	42—145°C/0·13 kPa, *Ib* : *IIb* : *IIIb* : *IVb* = = 0·5 : 7 : 1 : 4

[a] Determined by NMR spectroscopy. [b] The mixture contained also the unreacted starting sulphide and silicon hydride.

Triethyl/1-(vinylthio)ethyl/silane (Ia). ^{1}H-NMR spectrum: 0·64 (m) — CH_2Si, 0·98 (m) — CH_3CSi, 1·32 (m) — CH_3, 2·33 (m) — CHS, 5·08 — (=CH_b), 5·23 — (=CH_a), 6·28 — (=CH_c); $^3J_{CH-CH_3}$ = 7·2 Hz, $^3J_{bc}^{trans}$ = 16·4 Hz, $^3J_{ac}^{cis}$ = 10·0 Hz, $^2J_{ab}^{gem}$ < 0·5 Hz.

Triethyl/2-(vinylthio)ethyl/silane (IIa). ^{1}H-NMR spectrum: 0·57 (m) — CH_2Si, 0·86 (m) — CH_3CSi, 2·68 (m) — CH_2S, 4·95 — (=CH_b), 5·09 — (=CH_a), 6·28 — (=CH_c); $^3J_{bc}^{trans}$ = 16·7 Hz, $^3J_{ac}^{cis}$ = 10·2 Hz, $^2J_{ab}^{gem}$ < 0·5 Hz.

Triethyl(vinylthio)silane (IIIa). ^{1}H-NMR spectrum: 0·73 (m) — CH_2Si, 1·01 (m) — CH_3CSi, 5·30 — (=CH_a), 5·42 — (=CH_b), 6·20 — (=CH_c); $^3J_{bc}^{trans}$ = 16·2 Hz, $^3J_{ac}^{cis}$ = 9·0 Hz, $^2J_{ab}^{gem}$ = = 1·0 Hz.

Triethyl(ethylthio)silane (VIa). ^{1}H-NMR spectrum: 0·72 (m) — CH_2Si, 1·00 (m) — CH_3CSi, 1·27 (t) — CH_3CS, 2·43 (q) — CH_2S; $^3J_{SCH_2CH_3}$ = 7·0 Hz.

Triethyl-1-/3-(allylthio)propyl/silane (VIIa). n_D^{20} 1·4844, d_4^{20} 0·8841. ^{1}H-NMR spectrum: 0·52 (m) — CH_2Si, 0·92 (m) — CH_3SCi, 1·51 (m) — $SiCCH_2$, 2·98 (m) — (=CCH_2S), 5·02 (m) — (=CH_a and =CH_b), 5·74 (m) — (=CH_c); $^3J_{bc}^{trans}$ = 17·5 Hz, $^3J_{ac}^{cis}$ = 10·0 Hz, ^3J = CHCH$_2$S = = 7·0 Hz, $^4J_{SCH_2C=CH_a}$ = 1·0 Hz, $^2J_{ab}^{gem}$ = 1·0 Hz, $^3J_{SCH_2CH_2}$ = 7·0 Hz. The SCH$_2$CH=CH$_2$ protons which are the part ABC of the ABCX$_2$ spin system are assigned for an approximation of the first order spectra.

Triethyl(allylthio)silane (VIIIa). n_D^{20} 1·4790. ^{1}H-NMR spectrum: 0·74 (m) — CH_2Si, 0·99 (m) — CH_3CSi, 3·06 (d.t) — SCH_2, 4·97 (m) — (=CH_a), 5·11 (m) — (=CH_b), 5·76 (m) — (=CH_c); $^3J_{bc}^{trans}$ = 16·8 Hz, $^3J_{ac}^{cis}$ = 10·0 Hz, $^2J_{ab}^{gem}$ = 1·0 Hz, $^3J_{CH_2-CH_c}$ = 5·8 Hz, $^3J_{CH_2-CH_b}$ = 1·2 Hz, $^3J_{CH_2-CH_a}$ = 1·1 Hz.

TABLE III

Experimental Conditions for Reaction of Diallyl Sulphide with Triethyl- and Triethoxysilane
    For procedure see Experimental.

Silicon hydride mol . 10^3	Sulphide mol . 10^3	$H_2PtCl_6{}^a$ mol . 10^4	[RhCl{P(C$_6$H$_5$)$_3$}$_3$] mol . 10^7	h/°C
		$(CH_2=CH—CH_2)_2S$ + $(C_2H_5)_3SiH^{b,c}$		
9·9	9·9	5	—	2/100
14·2	14·2	—	15·4	8/120
		$(CH_2=CH—CH_2)_2S$ + $(C_2H_5O)_3SiH^{d,e}$		
5	5	5	—	6/120
5	5	—	5·3	6/120

^{a} Hexahydrate; 0·01M isopropanol solution. ^{b} The mixture obtained with chloroplatinic acid as catalyst contained 58·4% of *VIIa*, 4·4% of *IXa*. ^{c} The reaction mixture obtained with the use of the rhodium catalyst contained 10·0% of *IVa*, 6·5% of *VIIa*, 32·3% of *VIIIa*, 5·7% of *IXa*. ^{d} The mixture obtained with chloroplatinic acid contained 32·8% of *VIIb*, 15·0% of *Xb*. ^{e} The mixture obtained with the use of the rhodium catalyst contained 31·5% of *VIIb*, 8·3% of *Xb*, and 7·1% of (C$_2$H$_5$O)$_4$Si.

Triethyl-1-/3-*allylthio*-1-*propenyl*/*silane* (IXa). ^{1}H-NMR spectrum: 0·56 (m) — CH_2Si, 0·95 (m) — CH_3CSi, 2·97 (d.t) — (=CHCH$_2$S), 3·05 (d.t) — SiC=CCH$_2$, 5·01 (m) — (=CH$_a$ and =CH$_b$), 5·55 (d.t) — (=CH$_a$), 5·71 (m) — (=CH$_c$), 5·87 (d.t) — (=CH$_\beta$); $^3J^{trans}_{\alpha,\beta}$ = 18·0 Hz, $^3J_{=CH\beta CH_2S}$ = 6·0 Hz, $^3J_{=CH_cCH_2S}$ = 6·7 Hz, $^3J^{trans}_{bc}$ = 17·0 Hz, $^3J^{cis}_{ac}$ = 9·0 Hz, $^2J^{gem}_{ad}$ = 1·8 Hz, $^4J_{CH\alpha = CCH_2S}$ = 1 Hz, $^4J^{trans}_{CH_a = CCH_2S}$ = 1·0 Hz, $^4J^{cis}_{CH_b = CCH_2S}$ = 1·2 Hz.
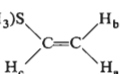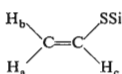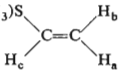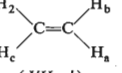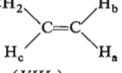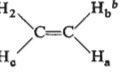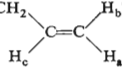
Triethoxy/1-(*vinylthio*)*ethyl*/*silane* (Ib). ^{1}H-NMR spectrum: 1·21 (t) — CH_3COSi, 1·29 (t) — CH_3, 2·23 (m) — CH, 3·84 (q) — CH_2O, 5·05 — (=CH$_b$), 5·11 — (=CH$_a$), 6·31 — (=CH$_c$); $^3J^{trans}_{bc}$ = 17·0 Hz, $^3J^{cis}_{ac}$ = 9·8 Hz, $^2J^{gem}_{ab}$ < 0·5 Hz, $^3J_{CH-CH_3}$ = 7·3 Hz, $^3J_{OCH_2CH_3}$ = 7·1 Hz.

Triethoxy/2-(*vinylthio*)*ethyl*/*silane* (IIb). H-NMR spectrum: 0·91 (m) — CH_2Si, 1·20 (m) — CH_3, 2·72 (m) — CH_2S, 3·78 (q) — OCH_2, 4·98 — (=CH$_b$), 5·10 — (=CH$_a$), 6·26 — (=CH$_c$); $^3J^{trans}_{bc}$ = 16·8 Hz, $^2J^{gem}_{ab}$ < 0·5 Hz, $^3J_{OCH_2CH_3}$ = 6·9 Hz, $^3J^{cis}_{ab}$ = 9·8 Hz.

Triethoxy(*vinylthio*)*silane* (IIIb). ^{1}H-NMR spectrum: 1·22 (t) — CH_3COSi, 3·85 (q) — CH_2O, 5·30 — (=CH$_a$), 5·42 — (=CH$_b$), 6·22 — (=CH$_c$); $^3J^{trans}_{bc}$ = 16·0 Hz, $^3J^{cis}_{ac}$ = 9·3 Hz, $^2J^{gem}_{ab}$ < < 0·5 Hz, $^3J_{OCH_2CH_3}$ = 7·5 Hz.

TABLE IV

Hydrosilylation, Cleavage and Hydrogenation Products Isolated from Reactions of Divinyl Sulphide and Diallyl Sulphide with Triethyl- and Triethoxysilane

Hydrosilylation[a]	Cleavage	Hydrogenation
$X_3SiCH(CH_3)S$ ... H$_b$, H$_c$ C=C H$_a$ (*Ia, b*)	H$_b$ ... SSiX$_3$ C=C H$_a$ H$_c$ (*IIIa, b*)	C_2H_5=SSi(X)$_3$ (*VIa, b*)
$X_3SiCH(CH_3)S$ ... H$_b$ C=C H$_a$ (*IIa, b*)	$(X_3Si)_2S$ (*IVa*)	C_2H_5SCH=CH$_2$ (*V*)
$X_3SiCH_2CH_2CH_2SCH_2$ ... H$_b$ C=C H$_a$ (*VIIa, b*)	X_3SiSCH_2 ... H$_b$ C=C H$_a$ (*VIIIa*)	
$X_3SiCH(CH_3)CH_2SCH_2$ ... H$_b$[b] C=C H$_a$ (*Xb*)	X_3SiCH=CHCH$_2SCH_2$ ... H$_b$[c] C=C H$_a$ (*IXa*)	

[a] X = C_2H_5 for *Ia—IVa* and *VIa—IXa*, X = C_2H_5O for *Ib—IIIb*, *VIb*, *VIIb* and *Xb*. [b] Ethyl vinyl sulphide was not detected. [c] Dehydrocondensation product (Eq. (*F*)).

Triethoxy-1-/3-(allylthio)propyl/silane (VIIb), n_D^{20} 1·4515, d_4^{20} 0·9640. ^{1}H-NMR spectrum: 0·61 (m) — CH_2Si, 1·26 (t) — CH_3, 1·60 (m) — CH_2CSi, 2·39 (t) — $SiCCCH_2$, 3·04 (t) — ($=CCH_2S$), 3·76 (q) — OCH_2, 5·02 (m) — ($=CH_a$ and $=CH_b$), 5·75 (m) — ($=CH_c$); $^3J_{bc}^{trans} = 18·0$ Hz, $^3J_{ac}^{cis} = 10·0$ Hz, $^2J_{ab}^{gem} = 2·0$ Hz, $^3J_{=CHCH_2S} = 7·0$ Hz, $^3J_{OCH_2CH_3} = 7·0$ Hz, $^3J_{SCH_2CH_2} = 8·0$ Hz, $^4J_{SCH_2C=CH_a} = 1·2$ Hz, $^4J_{SCH_2C=CH_b} = 0·8$ Hz.

Triethoxy-2-/3-(allylthio)propyl/silane (Xb), n_D^{20} 1·4525, d_4^{20} 0·9708. ^{1}H-NMR spectrum: 1·05 (m) — CH_3CSi, 1·19 (t) — CH_3COSi, 2·29 (m) — $CHSi$, 2·73 (m) — CH_2CSi, 3·02 (d.t) — ($=CCH_2S$) 3·78 (q) — CH_2OSi, 5·01 (m) — ($=CH_a$), 5·03 (m) — ($=CH_b$), 5·72 (m) — ($=CH_c$); $^3J_{bc}^{trans} = 17·5$ Hz, $^3J_{ac}^{cis} = 9·5$ Hz, $^3J_{OCH_2CH_3} = 7·0$ Hz, $^3J_{=CH_cCH_2S} = 7·0$ Hz, $^4J_{CH_b=CCH_2S} = 1·2$ Hz, $^4J_{CH_a=CCH_2S} = 0·8$ Hz.

Triethoxy(ethylthio)silane (VIb). ^{1}H-NMR spectrum: 1·20 (t) — CH_3COSi, 1·29 (t) — CH_3CS, 2·53 (q) — CH_2S, 3·82 (q) — CH_2O; $^3J_{SCH_2CH_3} = 7·5$ Hz, $^3J_{OCH_2CH_3} = 6·8$ Hz.

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Translated by J. Hetflejš.