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THE CATALYTIC REACTIONS OF TRIETHYL- AND TRIETHOXY-SILANE WITH UNSATURATED SULPHIDES

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Summary

The hydrosilylation of mono- and di-alkenyl sulphides of the type RS-$(CH_2)_nCH{=}CH_2$ (R = C_2H_5, $CH_2{=}CH$, $CH_2{=}CHCH_2$, C_3H_7, n = 0, 1 and 4) by triethyl- and triethoxy-silane, catalyzed by $H_2PtCl_6 \cdot 6\ H_2O$, $(Ph_3P)_3RhCl$ and $(PhCN)_2PdCl_2 \cdot Ph_3P$, has been studied. The addition of hydrosilane to the double bond of alkenyl sulphide leads to a mixture of two isomeric mono-adducts. The hydrosilane can cleave the C—S bond of the initial sulphides giving the corresponding derivatives of thiosilanes, $X_3SiS(CH_2)_nCH{=}CH_2$ (X = C_2H_5, C_2H_5O). Hydrosilylation of alkenyl sulphides is accompanied by some side reactions such as dehydrocondensation, reduction and polymerization. The effect of the catalyst nature, the structure of hydrosilane and alkenyl sulphide on the reaction route has been investigated.

Introduction

Hydrosilylation is the most common method for the preparation of carbofunctional organosilanes [1,2]. In particular, it is the means of synthesis of a series of organosilicon sulphur-containing monomers used as finishes for siliceous materials, as glass sizing agents, as intermediates for preparing ion-exchange polymers, as sorbents, etc. [3].

However, there are only limited reports on the hydrosilylation of unsaturated sulphides. According to Plueddemann [4], the addition of hydrosilanes, $HSiR_nX_{3-n}$, to dialkenyl sulphides, $CH_2{=}CH(CH_2)_nSCH{=}CH_2$, proceeds involving the double bond farthest from the sulphur atom. Hydrosilylation of the $CH_2{=}CH$ group in trialkyl(vinylthiomethyl)silane is accompanied by a number of side processes [5]. In contrast, diethylsilane and dialkylfluorosilanes add easily to divinyl [6,7] and diallyl sulphides [7].

The above data provoked us to investigate in more detail the effect of the structure of the initial unsaturated sulphide and hydrosilylating agent and the catalyst nature on the hydrosilylation process.

Results and discussion

In a typical example an equimolar mixture of alkenyl sulphide and hydrosilane was heated for an appropriate period of time in the presence of catalyst. The results are summarized in Table 1. It is seen from Table 1 that the reaction is non-selective for most of the sulphides studied and leads to the formation of the two structural isomers. The total yield of adducts and their ratios are seen to be sensitive to the structure of both the initial sulphide and the hydrosilylating agent. Thus the reaction of organosilanes with ethylvinyl sulphide gives a mixture of isomers in 37—48% yield.

$$C_2H_5SCH{=}CH_2 + X_3SiH \left\{ \begin{array}{l} \rightarrow \underset{\text{(Ia,b)}}{X_3SiCH(CH_3)SC_2H_5} \\ \rightarrow \underset{\text{(IIa,b)}}{X_3SiCH_2CH_2SC_2H_5} \end{array} \right.$$

(a, X = Et, b, X = EtO)

Isomer IIa, b is predominant in the presence of both H_2PtCl_6 and $(Ph_3P)_3RhCl$. The H_2PtCl_6-catalyzed reaction of the two silanes with divinyl sulphide gives a mixture of adducts in a considerably lower yield

$$CH_2{=}CHSCH{=}CH_2 + X_3SiH \left\{ \begin{array}{l} \rightarrow \underset{\text{(IIIa,b)}}{X_3SiCH(CH_3)SCH{=}CH_2} \\ \rightarrow \underset{\text{(IVa,b)}}{X_3SiCH_2CH_2SCH{=}CH_2} \end{array} \right.$$

The IIIa : IVa and IIIb : IVb ratios are 1 : 1 and 1 : 3, respectively. When the rhodium catalyst is used the isomeric adducts are formed in moderate yield only in the case of triethoxysilane with the β-isomer prevailing ($\alpha : \beta = 1 : 14$). Triethylsilane causes considerable cleavage of the =CH—S bond of the initial sulphide.

$$Et_3SiH + CH_2{=}CHSCH{=}CH_2 \rightarrow \underset{\text{(Va)}}{Et_3SiSCH{=}CH_2}$$

As far as the addition of Et_3SiH to the double bond of divinyl sulphide is concerned, it is negligible (the adduct yields do not exceed 5%). $Et_3SiSCH{=}CH_2$ may be the only reaction product at a shorter reaction time. These data indicate the influence of the catalyst nature on the reaction route. Cleavage of the C—S bond also occurs simultaneously with the hydrosilylation of divinyl sulphide when both silanes react with the above sulphide in the presence H_2PtCl_6.

The effect of the nature of the catalyst and the structure of the hydrosilylating agent on the route and rate of the reaction is especially well-displayed in the case of diallyl sulphide. The hydrosilylation of the latter by triethoxysilane in the presence of both platinum and rhodium catalysts is non-selective, leading to the formation of the two isomers.

$$(EtO)_3SiH + (CH_2{=}CHCH_2)_2S \left\{ \begin{array}{l} \rightarrow \underset{\text{(VIb)}}{(EtO)_3SiCH(CH_3)CH_2SCH_2CH{=}CH_2} \\ \rightarrow \underset{\text{(VIIb)}}{(EtO)_3SiCH_2CH_2CH_2SCH_2CH{=}CH_2} \end{array} \right.$$

TABLE 1

THE PRODUCTS OF THE REACTION OF ALKENYL SULPHIDES WITH HYDROSILANES

Initial sulphide	Silane	Products	Yield (%)	
			H_2PtCl_6	$(Ph_3P)_3RhCl$
$CH_2=CHSC_2H_5$	$(EtO)_3SiH$	$(EtO)_3SiCH(CH_3)SC_2H_5$	4.6	4.4
		$(EtO)_3SiCH_2CH_2SC_2H_5$	33.0	44.0
		$(EtO)_3SiSC_2H_5$	22.0	15.0
$CH_2=CHSCH=CH_2$ [a]	Et_3SiH	$Et_3SiCH(CH_3)SCH=CH_2$	10.9	
		$Et_3SiCH_2CH_2SCH=CH_2$	11.9	
		$Et_3SiSCH=CH_2$	27.0	27.0
		$Et_3SiSC_2H_5$	6.5	
$CH_2=CHSCH=CH_2$	$(EtO)_3SiH$	$(EtO)_3SiCH(CH_3)SCH=CH_2$	5.0	1.0
		$(EtO)_3SiCH_2CH_2SCH=CH_2$	15.0	14.0
		$(EtO)_3SiSCH=CH_2$	6.0	22.0
		$(EtO)_3SiSC_2H_5$	16.0	8.8
$(CH_2=CHCH_2)_2S$ [b]	Et_3SiH	$Et_3Si(CH_2)_3SCH_2CH=CH_2$	58.4	6.5
		$Et_3SiSCH_2CH=CH_2$	4.8	32.3
		$Et_3SiCH=CHCH_2SCH_2CH=CH_2$		5.7
$(CH_2=CHCH_2)_2S$ [c]	$(EtO)_3SiH$	$(EtO)_3SiCH(CH_3)$-$CH_2SCH_2CH=CH_2$	15.0	3.3
		$(EtO)_3SiCH_2CH_2CH_2SCH_2CH=CH_2$	32.8	31.6
$CH_2=CHCH_2SC_3H_7$	Et_3SiH	$Et_3SiCH_2(CH_2)CH_2SC_3H_7$		15.0
		$Et_3SiCH_2CH_2CH_2SC_3H_7$	82.0	24.0
		$Et_3SiSC_3H_7$	6.3	33.4
$CH_2=CHCH_2SC_3H_7$	$(EtO)_3SiH$	$(EtO)_3SiCH(CH_3)CH_2SC_3H_7$	22.0	
		$(EtO)_3SiCH_2CH_2CH_2SC_3H_7$	23.0	43.0
		$(EtO)_3SiSC_3H_7$	25.9	38.8
$CH_2=CH(CH_2)_4SC_2H_5$	Et_3SiH	$Et_3SiCH_2CH_2(CH_2)_4SC_2H_5$	26.0	9.0
$CH_2=CH(CH_2)_4SC_2H_5$	$(EtO)_3SiH$	$(EtO)_3SiCH(CH_3)(CH_2)_4SC_2H_5$	79.0	23.0

[a] Sulphide, 30 mmol, silane, 30 mmol, H_2PtCl_6, 5 × 10^{-3} mmol 150°C, 24 h; sulphide, 4.8 mmol, silane, 4.8 mmol, $(Ph_3P)_3RhCl$, 5 × 10^{-3} mmol, 120°C, 8 h. [b] Sulphide, 10 mmol, silane, 10 mmol, H_2PtCl_6, 5 × 10^{-3} mmol 100°C, 2 h; sulphide, 14.3 mmol, silane, 14.3 mmol, $(Ph_3P)_3RhCl$, 15 × 10^{-3} mmol, 120°C, 8 h.

[c] Sulphide, 5 mmol, silane, 5 mmol, H_2PtCl_6, 5 × 10^{-3} mmol 120°C, 6 h; sulphide, 5 mmol, silane, 5 mmol, $(Ph_3P)_3RhCl$, 5 × 10^{-4} mmol, 120°C, 6 h.

However the $\alpha : \beta$ isomer ratio increases when the rhodium catalyst is used (VIb : VIIb = 1 : 10 and 1 : 2 for the rhodium and platinum catalysts, respectively).

The H_2PtCl_6-catalyzed stereoselective hydrosilylation of diallyl sulphide by Et_3SiH proceeds in accordance with the Farmer rule. The yield of the cleavage product, $Et_3SiSCH_2CH=CH_2$, is very low. However, this silane mainly causes cleavage of the C—S bond in the presence of the rhodium catalyst. The terminal adduct is present in traces in the reaction mixture.

An unexpected reaction product is $Et_3SiCH=CHCH_2SCH_2CH=CH_2$, formed due to dehydrocondensation of Et_3SiH with initial sulphide. A similar process has been observed in the hydrosilylation of 1,4-butadiene [8].

We have found H_2PtCl_6 to be a better catalyst for the stereoselective hydrosilylation of allylpropyl sulphide by triethylsilane to afford only the terminal adduct, $Et_3Si(CH_2)_3SC_3H_7$. The rhodium catalyst is less active and decreases the selectivity of the process since β- and γ-isomers are formed. The reaction of the above sulphide with $(EtO)_3SiH$ catalyzed by H_2PtCl_6 also leads to isomeric adducts. Considerable amounts of the cleavage product, $X_3SiSC_3H_7$, are formed when the rhodium catalyst is used. Similarly to the case of ethylvinyl sulphide it is the S—alkenyl bond that undergoes cleavage, but not the $S—CH_2$ bond. Under the same conditions, no cleavage of diethyl and dipropyl sulphides by hydrosilanes occurs which proves the stability of the $S—CH_2$ bond.

Hydrosilylation of ethyl hexen-5-yl sulphide by X_3SiH is exclusively selective. Et_3SiH adds to the double bond according to the Farmer rule. In contrast, in the case of $(EtO)_3SiH$ an isomeric adduct is formed.

The influence of the catalyst nature on the reaction route of unsaturated sulphides with X_3SiH is clearly seen if $(PhCN)_2PdCl_2 \cdot Ph_3P$ is used. This catalyst, very efficient in the hydrosilylation of olefines [9,10], does not initiate the addition of X_3SiH to alkenyl sulphides. The main route is cleavage of the S—C bond of the initial sulphide. In this case Et_3SiH is the most reactive. Thus Et_3SiSEt, $Et_3SiSCH{=}CH_2$ and $Et_3SiSCH_2CH{=}CH_2$ are formed in 43, 22, and 15% yield, respectively. The yield of the products resulted from cleavage of alkenyl sulphides by $(EtO)_3SiH$ is only 2—3%.

The ethyl hexen-5-yl sulphide does not react with X_3SiH in the presence of the palladium catalyst.

The above data bear convincing evidence that cleavage of the S—C bond by hydrosilanes occurs in the case of sulphides containing a SCH= or $SCH_3CH{=}$ group where conjugation between vacant 3*d* orbitals of the sulphur atom and the π-electrons of the double bond is realised. This seems to be due to the increased electron density at the sulphur atom and the higher S—C bond polarity.

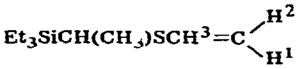
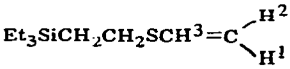
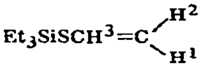
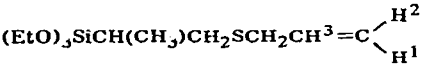
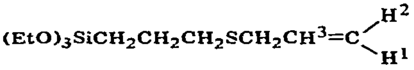
During the hydrosilylation of alkenyl sulphides by $(EtO)_3SiH$ the latter undergoes disproportionation to give $(EtO)_4Si$. The initial alkenyl sulphides may polymerize under the reaction conditions. Thus divinyl sulphide in the presence of newly prepared H_2PtCl_6 solution forms polymer products similar to those obtained under the effect of the Lewis acids [11].

Structure assignments

The assignment of the structures of the reaction products is based principally on their NMR data as shown in Table 2. The olefinic protons of the $SCH_2CH{=}CH_2$ fragment which are the ABC part of the $ABCX_2$ spin system are assigned for an approximation of the first order spectra. In the spectrum of $Et_3SiCH{=}CHCH_2SCH_2CH{=}CH_2$ there is an overlap of the multiplet of the H^4 and H^5 forming the AB part of the ABX_2 pattern and of the multiplet of H^3 which is the A part of the $ABCX_2$ spin system. Using the INDOR method the chemical shifts and coupling constants were measured for an approximation of the first order spectra. A triplet and quartet of CH_2S groups (2.45 ppm), as well as a multiplet of protons of other methylene groups between the Si and S atoms, have been observed in the ^1H NMR spectrum of $(EtO)_3SiCH(CH_3)(CH_2)_4SC_2H_5$. This proves the compound to be the product of addition rather than cleavage. This compound is most likely to have a non-linear structure since no $SiCH_2$-proton signal, commonly in the 0.5 ppm region, has been found in this case.

TABLE 2

NMR SPECTRAL DATA OF REACTION PRODUCTS

Compounds	δ(ppm)
$Et_3SiCH_2CH_2SEt$	0.60 (m, $SiCH_2CS$ and EtSi), 0.95 (m, MeCSi), 1.22 (t, MeCS), 2.48 (q, SCH_2C), 2.52 (m, SCH_2CSi)
Et_3SiSEt	0.72 (m, CH_2Si), 1.00 (m, MeCSi), 1.27 (t, MeCS), 2.43 (q, CH_2S)
$(EtO)_3SiCH(CH_3)SEt$	1.20 (t, MeCO and MeCS), 1.32 (m, MeCSi), 1.97 (m, SCHSi), 2.55 (q, CH_2S), 3.82 (q, CH_2O)
$(EtO)_3SiCH_2CH_2SEt$	0.83 (m, CH_2Si), 1.17 (t, MeCO and MeCS), 2.48 (q, CH_2S), 2.53 (m, SCH_2CSi), 3.77 (q, OCH_2)
$(EtO)_3SiSEt$	1.22 (t, MeCO), 1.30 (t, MeCS), 2.52 (q, CH_2S), 3.82 (q, OCH_2)
 $Et_3SiCH(CH_3)SCH^3{=}C\begin{smallmatrix}H^2\\H^1\end{smallmatrix}$	0.64 (m, CH_2Si), 0.98 (m, MeCSi), 1.32 (m, Me), 2.33 (m, CH), 5.08 ($=CH^2$), 5.13 ($=CH^1$), 6.28 ($=CH^3$), $^3J_{trans}(H^2{-}H^3) = 16.4$ Hz, $^3J_{cis}(H^1{-}H^3) = 10.0$ Hz, $^2J_{gem}(H^1{-}H^2) < 0.5$ Hz
 $Et_3SiCH_2CH_2SCH^3{=}C\begin{smallmatrix}H^2\\H^1\end{smallmatrix}$	0.57 (m, CH_2Si), 0.96 (m, MeCSi), 2.68 (m, CH_2S), 4.95 ($=CH^2$), 5.09 ($=CH^1$), 6.28 ($=CH^3$), $^3J_{trans}(H^2{-}H^3) = 16.7$ Hz, $^3J_{cis}(H^1{-}H^3) = 10.2$ Hz, $^2J_{gem}(H^1{-}H^2) < 0.5$ Hz
 $Et_3SiSCH^3{=}C\begin{smallmatrix}H^2\\H^1\end{smallmatrix}$	0.73 (m, CH_2Si), 1.01 (m, MeCSi), 5.30 ($=CH^1$), 5.42 ($=CH^2$), 6.20 ($=CH^3$), $^3J_{trans}(H^2{-}H^3) = 16.2$ Hz, $^3J_{cis}(H^1{-}H^3) = 9.0$ Hz, $^2J_{gem}(H^1{-}H^2) = 1.8$ Hz.
 $(EtO)_3SiCH(CH_3)CH_2SCH_2CH^3{=}C\begin{smallmatrix}H^2\\H^1\end{smallmatrix}$	1.05 (m, MeCSi), 1.19 (t, MeCOSi), 2.29 (m, CHSi), 2.73 (m, CH_2CSi), 3.02 (d.t., $=CCH_2S$), 3.78 (q, CH_2OSi), 5.01 (m, $=CH^1$), 5.03 (m, $=CH^2$), $^3J_{trans}(H^2{-}H^3) = 17.5$ Hz, $^3J_{cis}(H^1{-}H^3) = 9.5$ Hz, $^2J'_{gem}(H^1{-}H^2) = 2.3$ Hz
 $(EtO)_3SiCH_2CH_2CH_2SCH_2CH^3{=}C\begin{smallmatrix}H^2\\H^1\end{smallmatrix}$	0.61 (m, CH_2Si), 1.16 (t, CH_3), 1.60 (m, CH_2CSi), 2.39 (t, $SiCCCH_2$), 3.04 (d.t., $=CCH_2S$), 3.76 (q, OCH_2), 5.02 (m, $=CH^1$ and $=CH^2$), 5.75 ($=CH^3$), $^3J_{trans}(H^2{-}H^3) = 18.0$ Hz, $^3J_{cis}(H^1{-}H^3) = 10.0$ Hz, $^2J_{gem}(H^1{-}H^2) = 2.0$ Hz, $^3J(=CHCH_2S) = 7.0$ Hz, $^2J(SCH_2CH_2) = 8.0$ Hz
$Et^1_3SiCH^2_2CH^3_2CH^4_2SCH^5_2CH^6_2CH^7_3$	0.5 (m, CH_2SiCH_2), 0.93 (m, CH_3CSi), 1.0 (t, H^7), 1.51 (m, H^3 and H^6), 2.40 (t, H^4), 2.42 (t, H^5), $^3J(H^4{-}H^3) = {}^3J(H^5{-}H^6) = 7.0$ Hz
$Et_3SiSCH^3_2CH^2_2CH^1_3$	0.72 (m, CH_2Si), 1.00 (m, CH_3CSi), 1.10 (m, H^1), 1.58 (m, H^2), 2.34 (t, H^3), = $^3J(H^2{-}H^3) = 7.1$ Hz
$(EtO)_3SiCH(CH_3)CH_2SCH_2CH_2CH_3$	0.99 (t, CH_3CCS), 1.04 (d, CH_3CSi), 1.20 (t, CH_3CO), 1.82 (m, CH_2CS), 2.39 (t, CH_2S), 2.19 and 2.80 (m, CH_2CSi), 3.80 (q, OCH_2), $^3J(CH_3CH_2CS) = 7.5$ Hz, $^3J(CH_3CH) = 6.5$ Hz, $^3J(CH_3CH_2O) = 7.0$ Hz, $^2J(CH_2CSi) = 14$ Hz, $^3J(CHCH_2) = 4$ and 12 Hz
$(EtO)_3SiCH_2CH_2CH_2SC_3H_7$	0.5 (m, CH_2Si), 1.18 (t, CH_3CO), 1.6 (m, CH_2CS), 2.4 (m, CH_2CCSi), 3.76 (q, CH_2O), $^3J(CH_3CH_2O) = 7.0$ Hz

Experimental

All experiments were carried out in an argon atmosphere. The reactants were distilled in an argon atmosphere. Divinyl sulphide was freshly distilled.

GLC analysis of reaction mixtures was performed on a Chrom instrument equipped with a thermal-conductivity detector, using a 2.4 m × 4 mm column packed with 5% XE 60 Silicone on Chesasorb (45—60 mesh). The column temperature was programmed (4°C/min) from 80°C. Reaction mixtures were separated at 140°C by PGC (a 3.0 m × 10 mm column packed with 10% Lukopren G-1000 on Chromathon AW-HMDS was used for triethoxysilyl derivatives and a 3.0 m × 10 mm column with 15% Carbowax 20 M on Chromathon AW-HMDS was used for triethylsilyl derivatives). The compounds isolated by PGC were further used as authentic samples in GLC analyses. Yield determination was performed using the internal standard procedure.

The NMR spectra were measured on a Tesla Model BS 487C spectrometer operating at 80 MHz. 10% solutions of the substances in CCl_4 were used. Chemical shifts are given in ppm downfield from internal tetramethylsilane.

The reaction of alkenyl sulphides with hydrosilanes. These reactions were

TABLE 3

ANALYTICAL DATA FOR THE COMPOUNDS SYNTHESISED

Compounds	Analysis Found (calcd.) (%)			
	C	H	Si	S
$Et_3SiCH_2CH_2SEt$	59.05 (58.74)	11.94 (11.83)	13.03 (13.73)	15.23 (15.68)
Et_3SiSEt				18.08 (18.71)
$(EtO)_3SiCH(CH_3)SEt$	47.49 (47.59)	9.52 (9.58)	11.81 (11.12)	12.52 (12.71)
$(EtO)_3SiCH_2CH_2SEt$	47.72 (47.59)	9.86 (9.58)	10.22 (11.12)	13.73 (12.71)
$Et_3SiCH(CH_3)SCH=CH_2$	58.67 (59.33)	10.96 (10.95)	14.13 (13.87)	14.94 (15.83)
$Et_3SiSCH=CH_2$ [a]	54.87 (55.10)	10.50 (10.40)	15.93 (16.10)	18.15 (18.38)
$Et_3Si(CH_2)_3SCH_2CH=CH_2$ [b]	62.79 (62.53)	11.05 (11.37)	12.25 (12.18)	13.58 (13.91)
$Et_3SiSCH_2CH=CH_2$ [c]	57.21 (57.37)	10.64 (10.70)	15.22 (14.90)	17.08 (17.02)
$(EtO)_3SiCH(CH_3)CH_2SCH_2CH=CH_2$ [d]	51.48 (51.76)	9.35 (9.41)	11.47 (11.51)	9.60 (10.08)
$(EtO)_3Si(CH_2)_3SCH_2CH=CH_2$ [e]	50.87 (51.76)	9.41 (9.41)	11.53 (11.51)	9.55 (10.08)
$Et_3SiCH(CH_3)CH_2SC_3H_7$	62.87 (61.99)	12.06 (12.13)	10.07 (12.08)	14.50 (13.79)
$Et_3Si(CH_2)_3SC_3H_7$	61.98 (61.99)	12.37 (12.13)	12.09 (12.08)	13.61 (13.79)
$Et_3SiSC_3H_7$	55.78 (56.74)	11.19 (11.65)	14.90 (14.74)	14.84 (16.83)
$(EtO)_3SiCH(CH_3)CH_2SC_3H_7$	50.28 (51.36)	9.91 (10.06)	10.50 (10.01)	11.54 (11.43)
$(EtO)_3Si(CH_2)_3SC_3H_7$	51.93 (51.38)	10.38 (10.06)	9.98 (10.01)	11.73 (11.43)
$(EtO)_3SiSC_3H_7$	45.70 (45.34)	8.17 (9.30)	12.90 (11.78)	
$Et_3SiCH_2CH_2(CH_2)_4SC_2H_5$	65.32 (64.60)	11.92 (12.30)	10.78 (10.80)	11.62 (12.30)
$(EtO)_3SiCH(CH_3)(CH_2)_4SC_2H_5$	55.43 (54.54)	10.57 (10.39)	9.22 (9.09)	

[a] n_D^{20} 1.4725. [b] n_D^{20} 1.4844, d_4^{20} 0.8841. [c] n_D^{20} 1.4790. [d] n_D^{20} 1.4515, d_4^{20} 0.9640. [e] n_D^{20} 1.4525, d_4^{20} 0.9708.

carried out using the same method. The general procedure is outlined for the H_2PtCl_6-catalyzed hydrosilylation of ethylvinyl sulphide by triethylsilane. A mixture of 5.8 g (50 mmol) of Et_3SiH, 4.4 g (50 mmol) of $CH_2{=}CHSC_2H_5$ and 0.1 ml of 0.1 *M* of $H_2PtCl_6 \cdot 6\,H_2O$ solution in i-PrOH (5×10^{-5} mmol) was heated in a sealed ampule for 46 h at 150°C. The unreacted silane and sulphide were removed under reduced pressure. Vacuum distillation of the residue afforded 6.10 g of fraction, b.p. 40—90°C (3 mm), containing $Et_3SiCH(CH_3)SC_2H_5$ (2.5%), $Et_3SiCH_2CH_2SC_2H_5$ (41.0%) and $Et_3SiSC_2H_5$ (17.7%).

In other experiments, 50 mmol of sulphide and silane were usually used. The amount of $(Ph_3P)_3RhCl$ is 5×10^{-5} mmole. The exceptions are given in Table 1.

Analytical data are presented in Table 3.

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