



In the previous study<sup>4</sup> on the palladium(II)-catalysed hydrosilylation of 1,3-butadiene we found, however, that the structure of 1/1 adducts depends on the silicon hydride. Thus, for example, while the addition of triethoxysilane gave the 1/1 adduct postulated by the above authors, 1-triethoxysilyl-2-butene, the reactions of ethoxydipropyl- and diethoxypropylsilane led to terminal butenes, 4-ethoxydipropylsilyl- and diethoxypropylsilyl-1-butene, respectively. Unexpectedly, corresponding 1-alkoxyalkylsilyl-1,3-butadienes were formed as side products. This indicated that the reaction is more complex than proposed in Scheme 1. The fact that 4-silylsubstituted 1-butenes were obtained by reactions of silicon hydrides substituted with alkyl groups led us to reinvestigate hydrosilylation of 1,3-butadiene by trimethylsilane in relation to the formation and structure of 1/1 adduct(s). The aim of the study was to get more information concerning mechanism of the reaction.

## EXPERIMENTAL

### Compounds Used

1,3-Butadiene was of the same provenience as in the previous work<sup>4</sup>. Trimethylsilane was obtained in 60% yield by the reduction of trimethylchlorosilane with sodium-bis(2-methoxyethoxy)aluminium hydride<sup>5</sup>. Trimethyldeuteriosilane was prepared by the reduction of trimethylchlorosilane with lithium aluminium deuteride (62.5% yield, b.p. 7–10°; 85% isotopic purity by IR:  $\nu(\text{Si-D})$  1547  $\text{cm}^{-1}$  (Q-branch),  $\nu(\text{Si-H})$  2130  $\text{cm}^{-1}$ ). Palladium complexes, *trans*-PdCl<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>CN)<sub>2</sub> (ref.<sup>6</sup>), PdCl<sub>2</sub>(t-C<sub>4</sub>H<sub>9</sub>NC)<sub>2</sub>, PdCl<sub>2</sub>(cyclo-C<sub>6</sub>H<sub>11</sub>NC)<sub>2</sub>, PdCl(t-C<sub>4</sub>H<sub>9</sub>NC)P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>, PdCl(cyclo-C<sub>6</sub>H<sub>11</sub>NC)P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> (ref.<sup>7</sup>), PdCl<sub>2</sub>[P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sub>2</sub> (ref.<sup>8</sup>), and PdCl( $\pi$ -C<sub>3</sub>H<sub>5</sub>)<sub>2</sub> (ref.<sup>8</sup>) were prepared by reported procedures as indicated.

### Hydrosilylation of 1,3-Butadiene with Trimethylsilane

The procedure and g.l.c. analysis was reported in the previous work<sup>4</sup>. Samples of hydrosilylation products used as standards for analysis were obtained in the following way: 1-Trimethylsilyl-2,6-octadiene by fractional distillation, 4-trimethylsilyl-1-butene and 1-trimethylsilyl-1,3-butadiene by preparative gas chromatography using 360.06 cm column filled with 4% poly(ethylene-glycol adipate) on grinded unglazed tiles as a stationary phase (a 65°C oven temperature, a 20 ml/min hydrogen flow rate). 1,4-Bis(trimethylsilyl)-2-butene was obtained similarly (a 240 cm.06 cm column filled with 8.8% E 350 silicone elastomer on Chromaton N (0.2–0.25 mm), a 117°C oven temperature, a 20 ml/min hydrogen flow rate). The structure of the products was confirmed by IR, <sup>1</sup>H-NMR and mass spectra. The IR spectra in the 4000–400  $\text{cm}^{-1}$  region were recorded with a Zeiss, Model UR 20, double beam spectrophotometer (Jena, GDR) both for pure substances in capillary layers between KBr plates and for their approx. 5% solutions in spectrograde CCl<sub>4</sub> or CS<sub>2</sub> in 0.008 cm cells. The <sup>1</sup>H-NMR spectra were taken on a Tesla, Model BS-477, spectrometer working at 60 MHz. The mass spectra of 70 eV were measured with a spectrometer connected to a gas chromatograph of the type MS/GC-9000 (LKM, Sweden).

*4-Trimethylsilyl-1-butene.* For C<sub>7</sub>H<sub>16</sub>Si<sub>1</sub> (128.2) calculated: 65.53% C, 12.66% H; found: 65.55% C, 12.68% H. Mass spectrum: peaks at *m/e* 73 [(CH<sub>3</sub>)<sub>3</sub>Si<sup>+</sup>], 128 (molecule peak), and 113 [(M – 15)<sup>+</sup>]. IR spectrum:  $\nu(\text{CH}_2=\text{C})$  995  $\text{cm}^{-1}$ ,  $\gamma(\text{C}=\text{H})$  907  $\text{cm}^{-1}$ . The sample contained

7% of 1-trimethylsilyl-*trans*-2-butene which could not be separated by preparative gas chromatography.

*4-Trimethylsilyl-1-butene-d<sub>1</sub>*. Its IR spectrum was identical to the spectrum of undeuterated substance, except the band at  $2050\text{ cm}^{-1}$  which indicates the presence of deuterium on the carbon bonded in the chain by single C—C bond. Mass spectra at 70 and 13 eV shows peaks at  $m/e$  73  $[(\text{CH}_3)_3\text{Si}^+]$  and 129 (molecule peaks). From the numerical analysis<sup>9</sup> it follows that the dideuterated product could be present in the amounts less than 15%.

*1-Trimethylsilyl-1,3-butadiene*. For  $\text{C}_7\text{H}_{14}\text{Si}_1$  (126.2) calculated: 66.58% C, 11.17% H; found: 66.33% C, 11.14% H. Mass spectrum: peaks at  $m/e$  111  $[(M - 15)^+]$  and 126 (molecule peak). IR spectrum:  $\nu(\text{C}=\text{C})_{\text{conj.}}$   $1580\text{ cm}^{-1}$ .  $^1\text{H-NMR}$  spectrum (dioxane as internal standard — 2222.22 Hz): a singlet at 24.69 Hz  $[(\text{CH}_3)_3\text{Si}]$ , an unresolved multiplet at 421.94—320.11 Hz  $(\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-)$ . The sample obtained by the reaction of trimethyldeuteriosilane with 1,3-butadiene showed the same properties (deuterium was absent).

*1,4-Bis(trimethylsilyl)-2-butene*. Mass spectrum: molecule peak at  $m/e$  200. IR spectrum:  $\nu(\text{C}-\text{H})$   $3008\text{ cm}^{-1}$ ,  $\gamma(\text{HC}=\text{CH})_{\text{trans}}$   $961\text{ cm}^{-1}$ ,  $\nu(\text{C}=\text{C})$   $1635\text{ cm}^{-1}$  (very weak band).  $^1\text{H-NMR}$  spectrum benzene as internal standard — 2.59: a doublet at 9.82—9.84  $[(\text{CH}_3)_3\text{Si}]$ , 4.66  $\tau(\text{—CH}=\text{CH}-)$  a doublet at 8.40—8.54  $\tau(\text{—CH}_2-)$ . Retention time of the sample was identical to that of an authentic sample prepared<sup>10</sup> by hydrosilylation of 1,3-butadiene by trimethylsilane catalysed by  $\text{RhCl}[\text{P}(\text{C}_6\text{H}_5)_3]_3$ .

*1-Trimethylsilyl-2,6-octadiene*. For  $\text{C}_{11}\text{H}_{21}\text{Si}_1$  (182.4) calculated: 72.44% C, 12.16% H; found: 72.37% C, 12.12% H. Mass spectrum: peaks at  $m/e$  182 (molecule peak) and 127  $[(M - 55)^+]$ . IR spectrum:  $\nu(\text{CH}_3-\text{CH}=\text{C})$   $1390\text{ cm}^{-1}$ ,  $\nu(\text{C}=\text{C})$   $1658\text{ cm}^{-1}$ ,  $\nu(\text{C}-\text{H})$   $3010\text{ cm}^{-1}$ ,  $\gamma(\text{HC}=\text{CH})_{\text{trans}}$   $970\text{ cm}^{-1}$ . No band assignable to the terminal C=C bond.  $^1\text{H-NMR}$  spectrum (chloroform as internal standard): a singlet at 7.25 $\tau$   $(\text{CH}_3-\text{CH}=\text{C})$ , a multiplet at 4.55—4.65 $\tau$   $(\text{—CH}=\text{CH}-)$ , a quadruplet centered at 8.48 $\tau$   $(\text{—CH}_2-\text{CH}_2-)$ , a singlet at 2.74 $\tau$   $[(\text{CH}_3)_3\text{Si}]$ .

*1-Trimethylsilyl-2,6-octadiene-8-d<sub>1</sub>*. Mass spectrum was measured at 70 eV and 13 eV ionizing source to estimate the fragmentation of the substance to  $(M - 1)^+$  ions which could complicate the evaluation of intensities in the region of the molecule peak. It was found that the relative heights of the lines at both eV's are within  $\pm 5\%$ , i.e. the fragmentation to  $(M - 1)^+$  ions is negligible. The numerical analysis of molecule peaks  $M^+$  of the product due to combination of isotopes of hydrogen,  $^{13}\text{C}$  (1.3%) and  $^{29}\text{Si}$  (4%) (for details see<sup>9</sup>) further showed that a dideuterated compound formed by eventual C-H/Si-D exchange could be present in the amount less than 13%. The amount of undeuterated derivative (m.wt 182, 17) agreed with isotopic purity of the starting trimethyldeuteriosilane (85%). In addition to the peaks mentioned above the spectrum exhibited a peak at  $m/e$  129  $(M - 56)^+$  which was assigned to a  $\text{C}_4\text{H}_6\text{D}_1$  fragment  $(\text{DCH}_2-\text{CH}=\text{CH}-\text{CH}_2-)$ , inferred from IR and NMR spectra, see below). IR spectrum (in substantia): a medium band at  $3020\text{ cm}^{-1}$   $(\text{C}=\text{H})$ , a weak band at  $2050\text{ cm}^{-1}$   $(\text{C}-\text{D})$ , carbon bonded in the chain by single C—C bond), a weak band at  $1650\text{ cm}^{-1}$  (unconjugated C=C bonds), a medium band at  $1260\text{ cm}^{-1}$  and a strong one at  $850\text{ cm}^{-1}$   $[(\text{CH}_3)_3\text{Si}]$ . The absence of the bands at 3080 and  $910\text{ cm}^{-1}$  confirms that the compound does not contain the terminal C=C bond. The band at  $1360\text{ cm}^{-1}$  (compare the spectrum of undeuterated substance) is also absent, which indicates that deuterium is attached to the methyl group  $(-\text{CH}_2\text{D})$ .  $^1\text{H-NMR}$  spectra of the  $d_1$ -compound and undeuterated substance showed similar pattern, except the signal of the methyl group. A doublet at 8.42 $\tau$  observed in the spectrum of the former compound was assigned to the  $-\text{CH}_2\text{D}$  group, in accordance with the integral dependence.

## Other Reactions

*Hydrosilylation of 1,3-butadiene in the presence of 4-trimethylsilyl-1-butene.* A mixture of 4 mg (0.02 mmol) of  $[\text{PdCl}(\pi\text{-C}_3\text{H}_5)]_2$ , 0.6 ml (7.2 mmol) of the diene, 0.8 ml (7 mmol) of trimethylsilane, 2.0 ml (1.5 mmol) of 4-trimethylsilyl-1-butene, and 1.5 ml benzene was heated under argon in a sealed ampoule at  $100^\circ\text{C}$  for 4 h. As found by g.l.c. analysis, the ratios of 1-trimethylsilyl-1,3-butadiene and 1,4-bis(trimethylsilyl)-2-butene were within experimental errors identical to those obtained in the reaction carried out in the absence of the above compound.

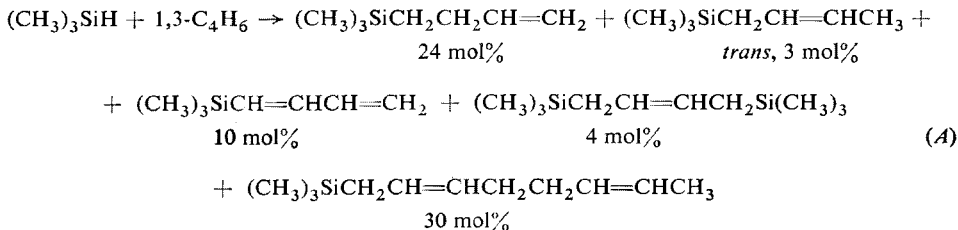
*Hydrosilylation of 4-trimethylsilyl-1-butene.* A mixture of 11.5 mg (0.03 mmol) of  $\text{PdCl}_2 \cdot (\text{C}_6\text{H}_5\text{CN})_2$ , 1.1 ml (8 mmol) of 4-trimethylsilyl-1-butene, 0.93 ml (8 mmol) of trimethylsilane, and 2 ml of benzene was heated in a sealed ampoule at  $100^\circ\text{C}$  for 4 h. As found by g.l.c., the silyl-butene did not react. The palladium complex was reduced to metallic palladium.

*Hydrosilylation of a mixture of 1/1 adducts.* A solution of 5.8 mg (0.015 mmol) of  $\text{PdCl}_2 \cdot (\text{C}_6\text{H}_5\text{CN})_2$ , 0.2 ml (1.7 mmol) of trimethylsilane, and 1 ml of a mixture of 1/1 adducts (containing 1.5 mmol of 1-trimethylsilyl-1,3-butadiene and 6 mmol of 4-trimethylsilyl-1-butene) in 2 ml of benzene was heated at  $100^\circ\text{C}$  for 4 h. By chromatographic analysis it was found that 1-trimethylsilyl-1,3-butadiene reacted with trimethylsilane (67% conversion) to give a compound with retention time which was identical to that of an authentic sample<sup>10</sup> of 1,4-bis-(trimethylsilyl)-2-butene.

*Isomerisation of 1-trimethylsilyl-cis-2-butene and 4-trimethylsilyl-1-butene.* A mixture of 7 mmol of 1-trimethylsilyl-cis-2-butene (4-trimethylsilyl-1-butene) and 0.03 mmol of  $\text{PdCl}_2(\text{C}_6\text{H}_5\text{CN})_2$  {0.02 mmol of  $[\text{PdCl}(\pi\text{-C}_3\text{H}_5)]_2$ } was heated in the absence and presence of benzene (1 ml) at  $100^\circ\text{C}$  for 4 h. G.l.c. analysis showed that the starting silylsubstituted compounds remained unchanged. The only reaction observed was the reduction of the palladium compounds to metallic palladium.

## RESULTS AND DISCUSSION

Preliminary experiments showed that the reaction of trimethylsilane with 1,3-butadiene is less selective at elevated temperatures than it was reported<sup>3</sup>. The products formed by the addition of trimethylsilane catalysed by  $\text{PdCl}_2(\text{C}_6\text{H}_5\text{CN})_2$  in benzene at  $100^\circ\text{C}$  can serve as an example (Equation (A)).



1-Trimethylsilyl-2-butene, *i.e.* the 1/1 adduct expected in accordance with Scheme 1, is present in only very small amounts. Similarly to the reactions of ethoxydipropyl- and diethoxypropylsilanes<sup>4</sup>, the addition yields the alkene with terminal C=C bond,

TABLE I

Hydrosilylation of 1,3-Butadiene by Trimethylsilane

B benzene, THF tetrahydrofuran; catalyst conc.  $3.5 \cdot 10^{-3}$  mol/mol  $(\text{CH}_3)_3\text{SiH}$ , the 1,3- $\text{C}_4\text{H}_6$  :  $(\text{CH}_3)_3\text{SiH}$  mol. ratio = 1.4 : 1, 0.3 ml solvent/mmol  $(\text{CH}_3)_3\text{SiH}$ .

Catalyst	°C/h solvent	Yields of adducts mol % <sup>a</sup>		Overall yield mol % <sup>a</sup>
		1/1	1/2	
$\text{PdCl}_2(\text{C}_6\text{H}_5\text{CN})_2$	22/24 (—)	6 (9)	35 (25)	41 (34)
	22/24 (B)	7 (10)	70 (49)	77 (59)
	100/4 (B)	27 (37)	42 (30)	69 (67)
$[\text{PdCl}(\pi\text{-C}_3\text{H}_5)]_2^b$	22/24 (—)	19 (27)	70 (49)	89 (76)
	100/4 (B)	26 (36)	48 (34)	74 (70)
$\text{PdCl}_2[\text{P}(\text{C}_6\text{H}_5)_3]_2^c$	100/4 (—)	3 (4)	76 (53)	79 (57)
	100/4 (B)	1 (2)	74 (51)	75 (53)
	100/4 (THF)	6 (8)	62 (44)	68 (52)
$\text{PdCl}_2(\text{C}_6\text{H}_{11}\text{NC})_2$	100/4 (B)	57 (68)	0	57 (68)
$\text{PdCl}_2(\text{t-C}_4\text{H}_9\text{NC})_2$	100/4 (B)	47 (57)	8 (6)	55 (63)
$\text{PdCl}_2[\text{C}_6\text{H}_{11}\text{NC}]\text{P}(\text{C}_6\text{H}_5)_3$	100/4 (B)	4 (6)	48 (34)	52 (40)
$\text{PdCl}_2(\text{t-C}_4\text{H}_9\text{NC})\text{P}(\text{C}_6\text{H}_5)_3$	100/4 (B)	2 (3)	56 (41)	58 (44)

<sup>a</sup> Based on 1,3-butadiene. The yields calculated with respect to the silicon hydride are given in parentheses. <sup>b</sup> Catalyst conc.  $1.75 \cdot 10^{-3}$  mol/mol  $(\text{CH}_3)_3\text{SiH}$ . <sup>c</sup> The complex reported<sup>3</sup> as ineffective for hydrosilylation carried out at 86°C for 6 h.

TABLE II

Composition of the Products of the Addition of Trimethylsilane to 1,3-Butadiene in Dependence on Reaction Time ( $\text{PdCl}_2(\text{C}_6\text{H}_5\text{CN})_2$ , 100°C, benzene)

Other conditions see Table I.

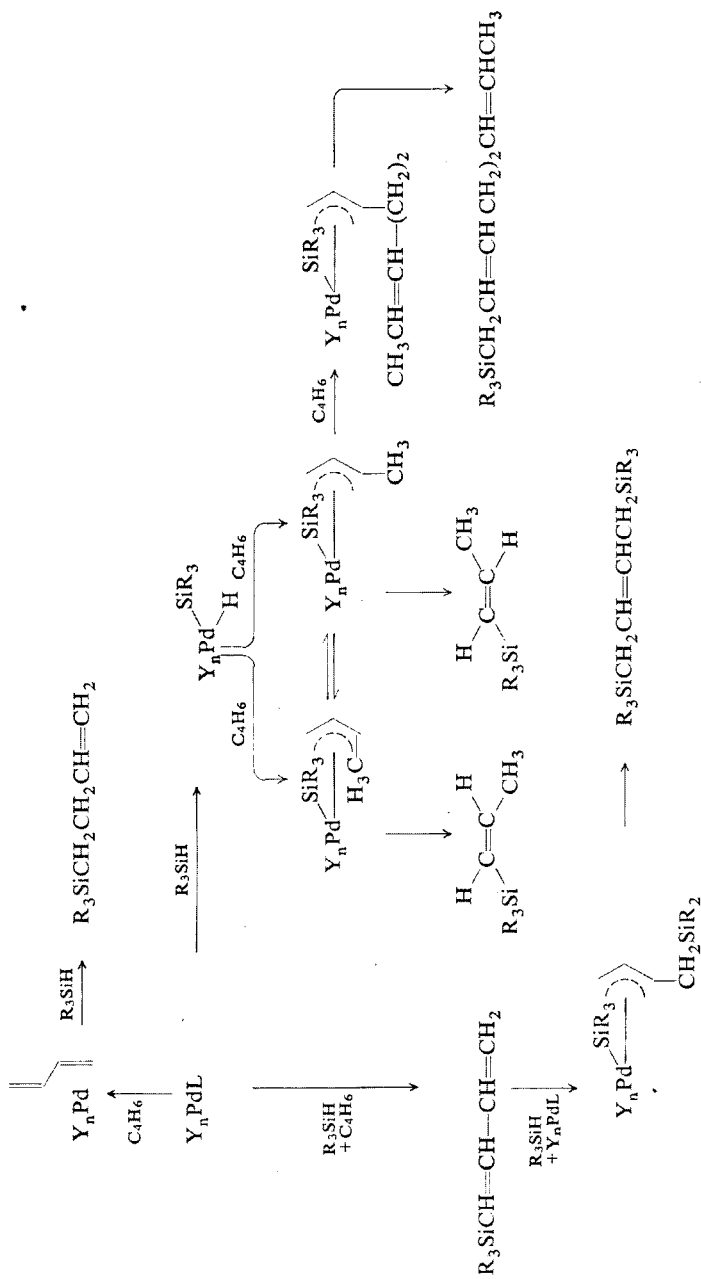
Time, h	Yields of adducts mol %		Overall yield mol % <sup>a</sup>
	1/1	1/2	
0.5	20	25	45
2.0	23	41	65
4.0	27	43	70
5.0	31	35	68
6.0	45	23	71

<sup>a</sup> With respect to 1,3-butadiene.

4-trimethylsilyl-1-butene. Usually major product of this addition, 1-trimethylsilyl-2,6-octadiene, and 4-trimethylsilyl-1-butene were formed in comparable amounts. Other silylsubstituted compounds produced by the reaction are 1-trimethylsilyl-1,3-butadiene and 1,4-bis(trimethylsilyl)-2-butene.

Several examples of the results obtained under various reaction conditions are shown in Table I. The changes in the amount of 1/1 adducts in dependence on temperature, solvent and catalyst are similar to those found for other silicon hydrides in the previous work<sup>4</sup> and comparable to the results reported by Takahashi and coworkers<sup>1-3</sup> for the addition of the same silicon hydride catalysed by a palladium(0) compound. From comparison of data obtained with the palladium-isonitrile complexes it follows that the introduction of one triphenylphosphine group as ligand markedly increases selectivity of the reaction with respect to formation of the 1/2 adduct. The same result is also achieved by using the reactants in suitable molar ratio ( $\text{PdCl}_2(\text{C}_6\text{H}_5\text{CN})_2$  100/4(B), see Table I – the 1,3- $\text{C}_4\text{H}_6/(\text{CH}_3)_3\text{SiH}$  molar ratio; 1/1 adduct (mol. %), 1/2 adduct (mol. %): 1.4, 37, 30: 2.0, 6, 83). None of the above factors influenced, however, the composition of 1/1 adducts. Thus, for example, the reactions carried out at 20–50°C produced the same compounds as at elevated temperatures, 4-trimethylsilyl-1-butene (with admixture of the *trans*-2-butene), 1-trimethylsilyl-1,3-butadiene and 1,4-bis(trimethylsilyl)-2-butene, in addition to the silyloctadiene. In the above temperature range the first three substances were present in the molar ratio 65 : 27 : 8 which remained essentially constant. As can be seen from Table II, 1/1 adducts [and 1,4-bis(trimethylsilyl)-2-butene] were formed already in the initial stage of the reaction. Their formation was preferred on prolonged reaction time. After 4 h, the overall yield did not increase, this being due to decreasing amount of the 1/2 adduct. At present this decrease is difficult to explain. By separate experiments we found that the 1/2 adduct does not react with trimethylsilane ( $\text{PdCl}_2(\text{C}_6\text{H}_5\text{CN})_2$  100°C, 6 h) to give a disilylated product and does not undergo decomposition to yield an 1/1 adduct or volatile substances detectable by gas-liquid chromatography. Also an octatriene has not been formed in this case, contrary to *e.g.* 1-methoxy-2,7-octadiene which decomposed on distillation of the reaction mixture containing  $\text{PdCl}_2(\text{C}_6\text{H}_5\text{CN})_2$  to give methanol and 1,3,7-octatriene<sup>11</sup>.

Several reactions carried out with the aim of explaining formation of 1/1 adducts confirmed that 1-trimethylsilyl-2-butene and 1-trimethylsilyl-1,3-butadiene do not arise from 4-trimethylsilyl-1-butene. We found that this compound is not dehydrogenated on heating at 100°C in the presence of  $\text{PdCl}_2(\text{C}_6\text{H}_5\text{CN})_2$  or  $[\text{PdCl}(\pi\text{-C}_3\text{H}_5)]_2$ , although some higher terminal olefins undergo this reaction under analogous conditions<sup>12</sup>. Furthermore, addition of 4-trimethylsilyl-1-butene to the initial reaction mixture did not result in an increase of the ratio of the silylsubstituted butadiene, and 1,4-bis(trimethylsilyl)-2-butene, to the silyloctadiene, compared to that obtained in the reaction carried out in the absence of this compound. Neither 4-trimethylsilyl-1-butene nor 1-trimethylsilyl-*cis*-2-butene were found to



SCHEME 2

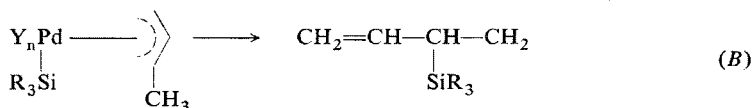
isomerise in the presence of palladium compounds, although isomerisations of several simple higher alkenes were accomplished under similar conditions<sup>13,14</sup>. Also hydrosilylation of 4-trimethylsilyl-1-butene by trimethylsilane in the presence of palladium complexes not containing phosphine ligands did not occur. 1,4-Bis(trimethylsilyl)butene, which would be formed by the above reaction, was further found unchanged on heating it in benzene with the palladium complexes (100/4 h). Its dehydrogenation to the bis-silyl derivative which is one of the products of the studied addition is thus excluded. It is worthy of note that formation of 1,4-disilylsubstituted 2-butene was observed only in those additions which led also to the silylbutadiene<sup>4</sup>. This indicated that the former compound could be formed by subsequent hydrosilylation of the latter derivative. Further experiments confirmed this assumption. The addition of 1-trimethylsilyl-1,3-butadiene (as a mixture of this compound (20% mol. %) and 4-trimethylsilyl-1-butene (80 mol. %)) to the initial reaction mixture increased the amount of the bis-trimethylsilylbutene in the expense of the silylbutadiene.

Additional support for the observations discussed above was provided by the results of the additions with the deuterated analogue,  $(\text{CH}_3)_3\text{SiD}$ . Their unambiguous interpretation was made possible by the fact that contrary to deuteration of 1,3-butadiene<sup>15</sup>, C—H/C—D exchange proceeds during hydrosilylation only to a negligible extent. We further found that also deuterium exchange between the silicon deuteride and products has not to be considered as important process. The products formed by the addition of trimethylsilane- $d_1$  to 1,3-butadiene were 4-trimethylsilyl-1-butene-3- $d_1$ , 1-trimethylsilyl-1,3-butadiene- $d_0$ , and 1-trimethylsilyl-2,6-octadiene-8- $d_1$ . The presence of undeuterated silylsubstituted butadiene speaks against its formation by dehydrogenation of 4-trimethylsilyl-1-butene, since in such a case an ascertainable amount of deuterium would have remained attached to the carbons of the conjugated system, even if considering H/D isotopic effect.

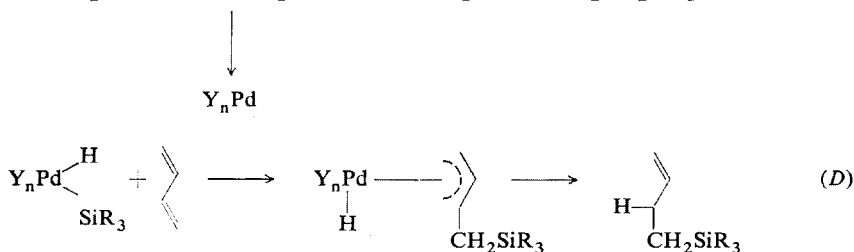
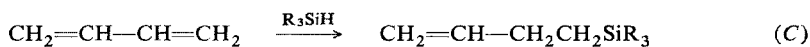
The location of deuterium in terminal silylsubstituted 1-butene and 2,6-octadiene provides information concerning the mechanism of the reaction. Before entering into its discussion we consider it useful to briefly summarise the results obtained with different silicon hydrides. Comparison of the reactivity of trichlorosilane, triethoxysilane, and trimethylsilane with the structure of their hydrosilylation products is illustrative. The addition of trichlorosilane proceeds at a fast rate even at room temperature<sup>16</sup>, giving selectively 1-trichlorosilyl-*cis*-2-butene. Triethoxysilane is less reactive than trichlorosilane. Its reaction with 1,3-butadiene at room temperature gives 1-triethoxysilyl-2,6-octadiene as a major product, 1-triethoxysilyl-*cis*-2-butene and the *trans* isomer are formed at elevated temperatures, the *trans*-2-butene not being produced by subsequent isomerisation of the *cis* isomer. By contrast to the above cases, the addition of trimethylsilane (and also ethoxydipropyl- and propyldiethoxysilane<sup>4</sup>) yields 1-silylsubstituted 1-butene in addition to the silyloctadiene, the above silicon hydrides being comparable in reactivity. As pointed out in the



previous work<sup>4</sup>, the formation of 1-silylsubstituted 2-butenes can be visualised by the scheme proposed by Takahashi and coworkers (Scheme 1). The absence of isomerisation reactions leads us to assume that the *cis*- and *trans*-isomers are directly formed from  $\pi$ -allyl intermediates, the equilibrium between *syn*- and *anti*-conformers<sup>17</sup> being dependent on the character of the silyl group (Scheme 2). Formation of the 1-silylsubstituted 1-butene is difficult to explain in terms of the suggested mechanism. This substance is the product of the 1,2-addition. The isomer with terminal C=C bond formed from the above  $\pi$ -allyl intermediate should be the 3-silylsubstituted 1-butene (Equation (B)). This compound has not been found among hydrosilylation products.



Two routes tentatively assumed to give the product obtained could involve the  $\pi$ -butadienyl intermediate (Equation (C)) and the  $\pi$ -allyl intermediate shown in Equation (D). Present results do not allow to differentiate between these possibilities. The 1,2-addition represented by Equation (C) is analogous to the additions of silicon hydrides to alkenes which do yield terminal silylsubstituted alkanes<sup>18,19</sup>. In view of the known instability of  $\pi$ -diene complexes of palladium which are readily converted to  $\pi$ -allyl complexes<sup>20</sup> this path would require essentially simultaneous attack of the silyl group and hydrogen on the C=C double bond. The second route involves the insertion of 1,3-butadiene to the Pd—Si bond, *i.e.* comparable lability of the silyl group and hydrogen. Unfortunately, there are no data on palladium-silyl complexes which can be offered in support of this assumption. With related Rh(I) and Pt(II) compounds it has been observed that the stability of silylhydrido complexes decreases in dependence on the nature of the silyl group in the order  $\text{Cl}_3\text{Si} > (\text{C}_2\text{H}_5\text{O})_3\text{Si} \gg (\text{CH}_3)_3\text{Si}$  (ref.<sup>21</sup>). It has been also reported<sup>22</sup> that the trimethylsilyl groups in the silyl-platinum(II) complex  $\text{Pt}[\text{Si}(\text{CH}_3)_3]_2$  (diphos) can be easily displaced by hydrogen.



The fact, that formation of the terminal butene was observed for the silicon hydrides with electronically dissimilar substituents makes the second path less probable. Of the other hydrosilylation products, 1-trimethylsilyl-1,3-butadiene may be formed by a substitution reaction, in accordance with the fact that the reaction of trimethyldeuteriosilane gives undeuterated product. A related reaction was observed in the hydrosilylation of ethylene by dichloromethylsilane<sup>23</sup>. The authors found that the reaction gives dichloromethylvinylsilane which did not result from dehydrogenation of the hydrosilylation product, dichloroethylmethylsilane. As already mentioned, the 1,4-disilylsubstituted 2-butene arises from subsequent hydrosilylation of the silylsubstituted butadiene. The formation of 1-trimethylsilyl-2,6-octadiene-8-*d*<sub>1</sub> supports the assumption that the reaction proceeds *via* a palladium hydride, as suggested by Takahashi and coworkers<sup>3</sup>. Although some of the steps remain to unambiguously confirm, we believe that the results obtained in the present and previous work can be rationalised by the following reaction scheme (Scheme 2).

## REFERENCES

1. Takahashi S., Shibano T., Hagihara N.: Chem. Commun. 1969, 161.
2. Hagihara N., Takahashi S., Shibano T.: Japan Pat. 7307, 416; Chem. Abstr. 79, 53532 (1973).
3. Takahashi S., Shibano T., Kojima H., Hagihara N.: Organometal. Chem. Syn. 1, 193 (1971/1972).
4. Langová J., Hettflejš J.: This Journal, in press.
5. Čapka M., Chvalovský V.: This Journal 34, 2785 (1969).
6. Kharash M. S., Seyler R. C., Mayo F. R.: J. Am. Chem. Soc. 60, 882 (1938).
7. Crociani B., Boschi T., Belluco U.: Inorg. Chem. 9, 2021 (1970).
8. Dent T., Long R., Wilkinson G.: J. Chem. Soc. 1964, 1585.
9. Langová J.: Thesis. Czechoslovak Academy of Sciences, Prague 1974.
10. Rejhon J., Hettflejš J.: Unpublished results.
11. Tsuji J.: Accounts Chem. Res. 6, 8 (1973).
12. Donati M., Conti F.: Tetrahedron Lett. 1966, 4953.
13. Sparke M. B., Turner L., Wenham A. J. M.: J. Catal. 4, 332 (1965).
14. Harrod J. F., Chalk A. J.: J. Am. Chem. Soc. 88, 3491 (1966).
15. Itatani H., Bailar J. C., jr: I & EC Product Research and Development 11, 147 (1962).
16. Vaisarová V., Čapka M., Hettflejš J.: Syn. Inorg. Metal-Org. Chem. 2, 289 (1972).
17. Keim W. in the book: *Transition Metals in Homogeneous Catalysis* (G. N. Schrauzer, Ed.), Chapter 3. Dekker, New York 1971.
18. Hara M., Ohno K., Tsuji J.: Chem. Commun. 1971, 247.
19. Tsuji J., Hara M., Ohno K.: German Offen. 1 942 798; Chem. Abstr. 73, 15497 (1970).
20. Maitlis P. M.: *The Organic Chemistry of Palladium*, Vol. I. Academic Press, New York 1971.
21. Cundy C. S., Kingston B. M., Lappert M. F.: Advan. Organometal. Chem. 11, 253 (1973).
22. Clemmit A. F., Glockling F.: Chem. Commun. 1970, 705.
23. Yoshihisa K., Kumada M., Tamao K., Umeno M.: J. Organometal. Chem. 50, 297 (1973).

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