

## HYDROSILYLATION OF 1,3-BUTADIENE CATALYSED BY PALLADIUM(II) COMPLEXES\* \*\*

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The addition of organosilicon hydrides  $(C_2H_5O)_n(n-C_3H_7)_{3-n}SiH$  ( $n = 0-3$ ),  $(t-C_4H_9O)_n \cdot (CH_3)_{3-n}SiH$  ( $n = 1-3$ ), and  $(CH_3)_n(neo-C_5H_{11})_{3-n}SiH$  ( $n = 0-2$ ) to 1,3-butadiene catalysed by  $PdCl_2L_2$  ( $L = C_6H_5CN, (C_6H_5)_3P$ ) and  $[PdCl(\pi-C_3H_5)]_2$  was studied. It was found that the reaction proceeds under mild conditions to give corresponding 1-silylsubstituted 2,6-octadienes (1/2 adducts), in addition to silylsubstituted butenes (1/1 adducts). The structure of 1/1 adducts depended on the structure of the silicon hydride. While the reaction of triethoxysilane gave a mixture of 1-silylsubstituted *cis*- and *trans*-2-butenes, the additions of diethoxypropyl- and ethoxydipropylsilane produced unexpectedly 4-silylsubstituted 1-butenes, along with 1-silylsubstituted 1,3-butadienes. Formation of these products as well as the effects of reaction conditions, silicon hydrides and catalysts are discussed in relation to the earlier proposed mechanism of the reaction.

It has recently been found that palladium(II) complexes are efficient catalysts for addition of organosilicon hydrides to conjugated dienes<sup>1-3</sup> (and references therein). In spite of this fact, only several examples of this reaction with the use of a very limited number of organosilicon hydrides (trimethylsilane, trichlorosilane, triethoxysilane<sup>4,5</sup>) have been reported thus far. Within the framework of a broader study of Pd(II)-catalysed hydrosilylation of 1,3-butadiene<sup>3-5</sup>, in the present work we were concerned with the effects of reaction conditions, the structure of silicon hydrides and catalysts on the course of the reaction.

### EXPERIMENTAL

The purity of all the compounds was checked by g.l.c., refractive index or by melting point determination (a Kofler hot stage microscope). The data obtained agreed with those reported. All manipulations with hydrolysable or oxygen-sensitive compounds were carried out with the exclusion of air.

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**1,3-Butadiene.** The diene was condensed and dried over a Nalsit 4 molecular sieve prior to using. Two commercial samples employed in this study (96%, Kaučuk Works, Kralupy /Vlt. and  $\geq 98\%$ , Fluka, Buchs) gave identical results.

**Organosilicon hydrides.**  $(n\text{-C}_3\text{H}_7)_3\text{SiH}$  (ref.<sup>6</sup>),  $(\text{CH}_3)_{3-n}(\text{neo-C}_5\text{H}_{11})_n\text{SiH}$  ( $n = 0-2$ , ref.<sup>7</sup>),  $(\text{C}_2\text{H}_5\text{O})_{3-n}(n\text{-C}_3\text{H}_7)_n\text{SiH}$  ( $n = 0-2$ , ref.<sup>8</sup>) and  $(t\text{-C}_4\text{H}_9\text{O})_{3-n}(\text{CH}_3)_n\text{SiH}$  ( $n = 1,2$ , ref.<sup>7</sup>) were prepared by reported procedures as indicated. Tri(tert-butoxysilane) was obtained in the following way. A total of 355 g (3.3 mol) of potassium tert-butanolate were added in small portions to a solution of 135.5 g (1 mol) of trichlorosilane in 750 ml of dry ether while maintaining the temperature of the reaction mixture within  $0-10^\circ\text{C}$ . Then the ether was replaced by benzene and the reaction mixture was refluxed for 3 h. Potassium chloride was removed by filtration and washed several times with benzene. The combined benzene extracts were distilled to give 56 g (0.23 mol, 22.5%) of the product, b.p.  $79-79.5^\circ\text{C}/16$  Torr,  $n_D^{25}$  1.3960 (ref.<sup>7</sup> records b.p.  $73^\circ\text{C}/15$  Torr,  $n_D^{25}$  1.3960).

**Palladium(II) compounds.**  $\text{trans-PdCl}_2(\text{C}_6\text{H}_5\text{CN})_2$  (ref.<sup>9</sup>),  $\text{PdCl}_2[\text{P}(\text{C}_6\text{H}_5)_2]_2$  (ref.<sup>10</sup>), and  $[\text{PdCl}(\pi\text{-C}_3\text{H}_5)]_2$  (ref.<sup>11</sup>) were synthesized by reported procedures as indicated.

**Hydrosilylation procedure.** All experiments were carried out in an inert atmosphere (argon or nitrogen) with degassed reactants and solvents. In manipulation with catalysts (*e.g.* in their transfer from Schlenk tubes to reaction flasks and during their weighing) their exposure to air oxygen was avoided. In a typical example, 8.44 mg (0.022 mmol) of  $\text{PdCl}_2(\text{C}_6\text{H}_5\text{CN})_2$  was weighed into a 5 ml. glass ampoule flushed out with nitrogen, then 1.35 ml of benzene were added and the mixture was cooled by a dry ice-ethanol bath. After addition of 0.6 ml (7.2 mmol) of 1,3-butadiene and 0.75 ml (4 mmol) of triethoxysilane, the ampoule was sealed and heated with shaking to a given temperature which was maintained with an accuracy of  $\pm 0.2^\circ\text{C}$  for a given reaction time. Each experiment was repeated at least twice. When the results obtained differed more than by 10 rel.% (max. 15% rel.%), additional runs were performed and the results were averaged. G.l.c. analysis of reaction mixtures was performed on a Chrom 3 chromatograph equipped with a thermal-conductivity detector, using 2.4 m. 4 mm column filled with 11.5% E 302 silicone elastomer on Chromosorb W (30-60 mesh). The flow rate of the carrier gas hydrogen was 22 ml/min and the column temperature was programmed ( $6^\circ\text{C}/\text{min}$ ) in dependence on the composition of reaction mixtures:  $50-170^\circ\text{C}$  in the case of the triethoxysilane-1,3-butadiene reaction,  $50-190^\circ\text{C}$  for analysis of the mixtures produced by additions of the ethoxypropylsilanes  $(\text{C}_2\text{H}_5\text{O})_{3-n}(n\text{-C}_3\text{H}_7)_n\text{SiH}$  ( $n = 1-3$ ) and tert-butoxymethylsilanes  $(t\text{-C}_4\text{H}_9\text{O})_{3-n}(\text{CH}_3)_n\text{SiH}$  ( $n = 1-3$ ), and  $50-230^\circ\text{C}$  for the additions of methylncopentylsilanes  $(\text{CH}_3)_{3-n}(\text{neo-C}_5\text{H}_{11})_n\text{SiH}$  ( $n = 0-2$ ). A mixture of butenylsilanes (1 : 1 adducts) formed in the additions of triethoxy-, ethoxydiethyl-, and diethoxypropylsilane was analyzed on a capillary column (50 m  $\times$  0.25 mm) filled with tricresyl phosphate (a  $120^\circ\text{C}$  column temperature). The percentual amount of the individual reaction products in reaction mixtures was calculated from corresponding peak areas in the usual way<sup>12</sup> (for details see ref.<sup>13</sup>).

**Hydrosilylation products.** As found by g.l.c. analysis, hydrosilylation of 1,3-butadiene by the above organosilicon hydrides gives products of two types: silylsubstituted octadienes (1/2 adducts) and silylsubstituted butenes (1/1 adducts). While 1/2 adducts could be easily isolated by fractional distillation as pure compounds, 1/1 adducts were found to be a mixture of isomers with very close boiling points. Some of these isomers were obtained pure by preparative gas chromatography. The reaction conditions used to prepare the above compounds for purposes of their characterization are shown in Table I. The compounds obtained were further used as authentic samples in g.l.c. analyses of the composition of reaction mixtures after hydrosilylation. Physical properties

and elemental analyses for hydrosilylation products listed in Table I are given in Table II. The structure of the products was confirmed by IR and NMR spectroscopy. The IR spectra were recorded with a Zeiss, Model UR 20, double beam spectrophotometer (Jena, GDR) in the 4000 to 400  $\text{cm}^{-1}$  region both for pure substances in capillary layers between KBr plates and for their approx. 5% solutions in spectrograde  $\text{CCl}_4$  or  $\text{CS}_2$  in 0.008 cm NaCl cells. The  $^1\text{H}$  NMR spectra were taken on a Tesla, Model BS-477, spectrometer working at 60 MHz. The IR spectra of all

TABLE I

Reaction Conditions Used for Preparative Hydrosilylation of 1,3-Butadiene by Various Organosilicon Hydrides and Hydrosilylation Products Isolated

15 mmol  $\text{R}_3\text{SiH}$ ; the 1,3- $\text{C}_4\text{H}_6$  :  $\text{R}_3\text{SiH}$  molar ratio 1.8 : 1.

| $\text{R}_3\text{SiH}$<br>( $^\circ\text{C}/\text{h}$ )                                    | Catalyst:<br><i>c.</i> $10^{3 \cdot a}$  | Product  | Yield<br>% <sup>b</sup> |
|--|--|--|-------------------------|
| $(n\text{-C}_3\text{H}_7)_3\text{SiH}$<br>(100/4)  | $\text{PdCl}_2[\text{P}(\text{C}_6\text{H}_5)_3]_2$<br>4.33  | 1-tripropylsilyl-2,6-octadiene (I)   | 62                      |
| $\text{C}_2\text{H}_5\text{O}(n\text{-C}_3\text{H}_7)_2\text{SiH}$<br>(22/24)<br>(100/4)   | $[\text{PdCl}(\pi\text{-C}_3\text{H}_5)]_2$<br>2.75<br>2.75  | 1-ethoxydipropylsilyl-2,6-octadiene (II)<br>4-ethoxydipropylsilyl-1-butene <sup>c</sup>  | 86<br>69                |
| $(\text{C}_2\text{H}_5\text{O})_2(n\text{-C}_3\text{H}_7)\text{SiH}$<br>(22/24)<br>(100/4) | $[\text{PdCl}(\pi\text{-C}_3\text{H}_5)]_2$<br>2.75<br>2.75  | 1-diethoxypropylsilyl-2,6-octadiene (III)<br>4-diethoxypropylsilyl-1-butene <sup>d</sup>   | 83<br>89                |
| $(\text{C}_2\text{H}_5\text{O})_3\text{SiH}$<br>(22/24)<br>(100/4)<br>(100/4)              | $\text{PdCl}_2(\text{C}_6\text{H}_5\text{CN})_2$<br>5.5<br>$[\text{PdCl}(\pi\text{-C}_3\text{H}_5)]_2$<br>2.75<br>$\text{PdCl}_2[\text{P}(\text{C}_6\text{H}_5)_3]_2$<br>5.5 | 1-triethoxysilyl-2,6-octadiene (IV)<br>1-triethoxysilyl-2-butene<br>( <i>cis/trans</i> = 1 : 2.3)<br>1-triethoxysilyl-2-butene<br>( <i>cis/trans</i> = 10 : 1) | 84<br>85<br>63          |
| $(\text{CH}_3)_2(\text{t-C}_4\text{H}_9\text{O})\text{SiH}$<br>(22/24)                     | $[\text{PdCl}(\pi\text{-C}_3\text{H}_5)]_2$<br>2.75  | 1-dimethyl-tert-butoxysilyl-2,6-octadiene (V)  | 90                      |
| $(\text{CH}_3)(\text{t-C}_4\text{H}_9\text{O}_2)\text{SiH}$<br>(22/24)                     | $\text{PdCl}_2(\text{C}_6\text{H}_5\text{CN})_2$<br>5.5  | 1-methyl-di-tert-butoxysilyl-2,6-octadiene (VI)  | 89                      |
| $(\text{CH}_3)_2(\text{neoC}_5\text{H}_{11})\text{SiH}$<br>(22/24)                         | $\text{PdCl}_2(\text{C}_6\text{H}_5\text{CN})_2$<br>5.5  | 1-dimethylneopentylsilyl-2,6-octadiene (VII)   | 90                      |
| $(\text{CH}_3)(\text{neoC}_5\text{H}_{11})_2\text{SiH}$<br>(22/24)                         | $[\text{PdCl}(\pi\text{-C}_3\text{H}_5)]_2$<br>2.75  | 1-methyldineopentylsilyl-2,6-octadiene (VIII)  | 96                      |

<sup>a</sup> *c* mol catalyst/mol  $\text{R}_3\text{SiH}$ . <sup>b</sup> Calculated with respect to 1,3-butadiene. <sup>c</sup> Containing approx. 15 mol.% of 1-(ethoxydipropylsilyl)-1,3-butadiene. <sup>d</sup> Containing approx. 15 mol.% of 1-(diethoxypropylsilyl)-1,3-butadiene.

the silyloctadienes showed the absorption bands due to two unconjugated internal double bonds ( $\text{C}=\text{C}$ )  $1658\text{ cm}^{-1}$  and ( $\text{H}-\text{C}=\text{C}$ )  $3020\text{ cm}^{-1}$ . The band for a terminal  $\text{C}=\text{C}$  bond was absent. The presence of several  $\text{C}-\text{C}$  and  $\text{Si}-\text{C}$  bonds in products did not allow to determine unambiguously the configuration of  $\text{C}=\text{C}$  disubstituted bonds. The band for the *trans* arrangement was masked by the bands arising from the  $\text{C}-\text{C}$  stretching vibrations, and the bands which are characteristic of the *cis* arrangement coincided with the bands due to the stretching vibrations of the  $\text{Si}-\text{C}_4$  skeleton. The NMR spectra of all these compounds showed similar patterns: a singlet ("long range coupling") at  $7.90\tau$  for ( $\text{CH}_3-\text{C}=\text{C}$ ), an unsymmetrical quadruplet at  $8.3-8.6\tau$  for ( $-\text{CH}_2-\text{CH}_2-$ ), an unsymmetrical multiplet at  $4.58\tau$  for ( $-\text{CH}=\text{CH}-$ ) bonds, and a multiplet in the  $8.31-9.55\tau$  region for trisubstituted silyl groups, the residence of which depended on the structure of the silyl group. On the basis of these data and the similarity of the NMR spectra with the spectrum reported for 1-trimethylsilyl-2,6-octadiene by Takahashi and coworkers<sup>1</sup>, the 1/2 adducts obtained in the present work were assigned the structure of 1-silylsubstituted 2,6-octadienes. The structure of pure 1/1 adducts was confirmed similarly. In some cases attempted isolation of single isomers from reaction mixture by preparative gas chromatography has failed. In those

TABLE II  
Physical Properties and Elemental Analyses for Hydrosilylation Products

| Compound        | Formula<br>(m.wt.)   | Calculated/Found |       | B.p., °C/Torr<br>$n_D^{20}$ |
|-----------------|--|------------------|-------|-----------------------------|
|                 |  | % C              | % H   |                             |
| I               | $\text{C}_{17}\text{H}_{34}\text{Si}_1$<br>(266.5)           | 76.60            | 12.86 | 160—161/14                  |
|                 |  | 76.31            | 12.70 | 1.4629                      |
| II              | $\text{C}_{16}\text{H}_{32}\text{O}_1\text{Si}_1$<br>(268.3) | 71.50            | 12.00 | 113—114/5                   |
|                 |  | 71.49            | 12.02 | 1.4434                      |
| III             | $\text{C}_{15}\text{H}_{30}\text{O}_2\text{Si}_1$<br>(270.5) | 66.61            | 11.10 | 88.5—89.0/1                 |
|                 |  | 66.50            | 11.12 | 1.4457                      |
| IV <sup>a</sup> | $\text{C}_{14}\text{H}_{28}\text{O}_3\text{Si}_1$<br>(272.4) | 61.71            | 10.36 | 87—88/2                     |
|                 |  | 61.77            | 10.37 | 1.4340                      |
| V               | $\text{C}_{14}\text{H}_{28}\text{O}_1\text{Si}_1$<br>(240.5) | 69.93            | 11.74 | 126—127/10                  |
|                 |  | 69.05            | 11.84 | 1.4439                      |
| VI              | $\text{C}_{17}\text{H}_{34}\text{O}_2\text{Si}_1$<br>(298.5) | 68.39            | 11.48 | 78—79/1                     |
|                 |  | 68.16            | 11.29 | 1.4389                      |
| VII             | $\text{C}_{15}\text{H}_{30}\text{Si}_1$<br>(238.5)           | 75.54            | 12.68 | 70—72/2                     |
|                 |  | 75.07            | 12.67 | 1.4607                      |
| VIII            | $\text{C}_{19}\text{H}_{38}\text{Si}_1$<br>(294.6)           | 77.46            | 13.00 | — <sup>b</sup>              |
|                 |  | 77.21            | 12.97 | 1.4674                      |

<sup>a</sup> 1-Triethoxysilyl-*cis*-2-butene (obtained by preparative gas chromatography (2.4 m × 0.6 cm column filled with 7.5% Apiezon L + 7.5% Benton 34 on Celit 545; 20 ml  $\text{H}_2$ /min, a 120°C oven temperature) from a mixture of the *cis* and *trans* isomer (10 : 1, Table I)]. For  $\text{C}_{10}\text{H}_{22}\text{O}_3\text{Si}_1$  (218.3) calculated: 54.97% C, 10.16% H; found: 54.78% C, 10.13% H;  $n_D^{20}$  1.4149. <sup>b</sup> Obtained by preparative gas chromatography (2.4 m × 0.6 cm column filled with 8.8% E 350 silicone elastomer on Chromaton N (0.2—0.25 mm particle size), 20 ml  $\text{H}_2$ /min, a 210°C oven temperature).

cases the presence of individual isomers was inferred from the IR spectra of reaction mixtures, using the method described earlier<sup>14</sup>. By combined gas chromatographic and IR analysis, 1/1 adducts formed by the reactions of dipropylethoxy- and propyldiethoxysilane with 1,3-butadiene were identified as a mixture of 4-ethoxydipropylsilyl-1-butene and 1-ethoxydipropylsilyl-1,3-butadiene (approx. 6 : 1), and of 4-diethoxypropylsilyl-1-butene and 1-diethoxypropylsilyl-1,3-butadiene (approx. 5.5 : 1). In both cases a small amount of corresponding *cis*- and *trans*-2-butenes was also detected. The IR spectra showed two absorption bands in the region of the C—H stretching vibrations (at 3020 and 3080 cm<sup>-1</sup>), three bands in the region of the C=C bond vibrations (at 1630, 1645, and 1670 cm<sup>-1</sup>) which confirm the presence of the terminal carbon-carbon double bond, and two different internal C=C bonds (the *cis* and *trans* isomer) and a band at 1580 cm<sup>-1</sup> which is characteristic of conjugated double bonds. Analogous reaction of triethoxysilane gave a mixture of 1/1 adducts consisting of 1-triethoxysilyl-*cis*-2-butene and -*trans*-2-butene as major products, with admixture of 4-triethoxysilyl-1-butene. The last compound could be separated from the *trans* isomer only on a capillary column.

TABLE III

Hydrosilylation of 1,3-Butadiene by Triethoxysilane in the Absence and Presence of Solvents of Different Polarity (Benzene B, Tetrahydrofuran THF)

Catalyst conc.  $5.5 \cdot 10^{-3}$  mol/mol R<sub>3</sub>SiH, the 1,3-C<sub>4</sub>H<sub>6</sub> : R<sub>3</sub>SiH molar ratio = 1.8 : 1, 0.4 ml solvent/mmol R<sub>3</sub>SiH.

| Catalyst  | °C/h<br>(solvent) | Yields of adducts |         | Overall<br>yield<br>mol.% <sup>a</sup> |
|---|-------------------|-------------------|---------|--|
|   |                   | 1/1               | 1/2     |  |
| PdCl <sub>2</sub> (C <sub>6</sub> H <sub>5</sub> CN) <sub>2</sub>                             | 22/24 (—)         | 9 (16)            | 91 (82) | 100 (98)                               |
|   | 22/24 (B)         | 6 (11)            | 93 (84) | 99 (95)                                |
|   | 22/24 (THF)       | 2 (3)             | 67 (60) | 69 (63)                                |
|   | 100/4 (—)         | 16 (29)           | 32 (27) | 48 (66)                                |
|   | 100/4 (B)         | 15 (27)           | 51 (46) | 66 (73)                                |
|   | 100/4 (THF)       | 3 (6)             | 41 (37) | 44 (43)                                |
| [PdCl(π-C <sub>3</sub> H <sub>5</sub> ) <sub>2</sub> ] <sup>b</sup>                           | 22/24 (—)         | 8 (15)            | 92 (83) | 100 (98)                               |
|   | 22/24 (B)         | 8 (15)            | 92 (83) | 100 (98)                               |
|   | 22/24 (THF)       | 5 (9)             | 91 (82) | 96 (91)                                |
|   | 100/4 (—)         | 45 (81)           | 20 (18) | 65 (99)                                |
|   | 100/4 (B)         | 15 (23)           | 63 (57) | 78 (80)                                |
|   | 100/4 (THF)       | 8 (14)            | 60 (54) | 68 (68)                                |
| PdCl <sub>2</sub> [P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>2</sub> <sup>c</sup> | 100/4 (—)         | 35 (63)           | 38 (35) | 73 (98)                                |
|   | 100/4 (B)         | 14 (24)           | 12 (11) | 26 (35)                                |
|   | 100/4 (THF)       | 1 (2)             | 8 (7)   | 9 (9)                                  |

<sup>a</sup> With respect to 1,3-butadiene. The yields based on the hydride are given in parentheses. <sup>b</sup> Catalyst conc.  $2.75 \times 10^{-3}$  mol/mol R<sub>3</sub>SiH. <sup>c</sup> Because of poor solubility of the complex, 1 ml solvent was used per 1 mmol R<sub>3</sub>SiH.

## RESULTS AND DISCUSSION

Hydrosilylation of 1,3-butadiene catalysed by Pd(II) complexes can lead in general to the products of two types<sup>1,3</sup>: silylsubstituted butenes (1/1 adducts) and silylsubstituted octadienes (1/2 adducts). The relative amount of both products can be expected to be influenced by several factors: the structure of silicon hydrides, reaction conditions and the structure of Pd(II) complexes used as catalysts. In order to examine the effect of these factors in more detail we carried out hydrosilylations of this diene with three series of organosilicon hydrides ( $(C_2H_5O)_n(n-C_3H_7)_{3-n}SiH$  ( $n = 0-3$ ),  $(t-C_4H_9O)_n(CH_3)_{3-n}SiH$  ( $n = 1-3$ ), and  $(CH_3)_n(neoC_5H_{11})_{3-n}SiH$  ( $n = 2-0$ )) of which two contained derivatives substituted with bulky, sterically demanding groups. Several palladium(II) complexes which were already found to be efficient for hydrosilylation of the diene by trimethyl- and trichlorosilane<sup>3,5</sup>, were chosen as catalysts (Table III). All experiments were quantitatively evaluated both with respect to the starting organosilicon hydride and with respect to the diene. If major products were 1/2 adducts the results related to the diene are discussed, since this substance was present in substoichiometric amount. On the contrary, in cases where 1/1 adducts predominated, discussion is based on the results determined with respect to the organosilicon hydride.

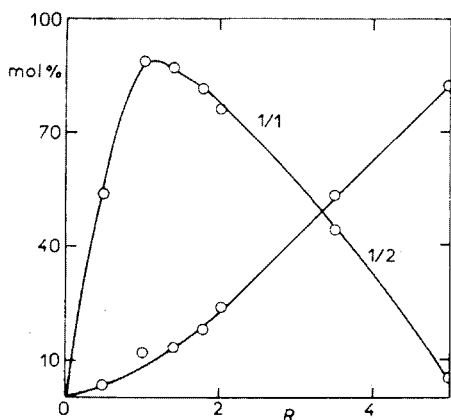


FIG. 1

Dependence of the Yields of 1/1 and 1/2 Adducts on the 1,3-Butadiene to Triethoxysilane Ratio ( $R$ ) for the Hydrosilylation Catalysed by  $[PdCl(\pi-C_3H_5)]_2$  in the Absence of Solvent

Catalyst conc.  $2.75 \cdot 10^{-3}$  mol/mol  
 $(C_2H_5O)_3SiH$ ,  $100^\circ C$ , 4 h.

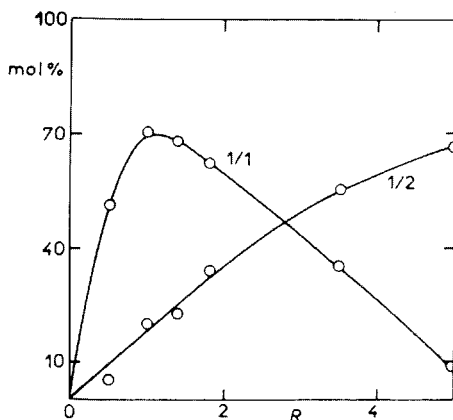


FIG. 2

Dependence of the Yields of 1/1 and 1/2 Adducts on the 1,3-Butadiene to Triethoxysilane Ratio ( $R$ ) for the Hydrosilylation Catalysed by  $PdCl_2[P(C_6H_5)_3]_2$  in the Absence of Solvent

Catalyst conc.  $5.5 \cdot 10^{-3}$  mol/mol  
 $(C_2H_5O)_3SiH$ ,  $100^\circ C$ , 4 h.

The effect of reaction conditions on the course of the addition of triethoxysilane to 1,3-butadiene is shown in Table III and Figs 1–3. As can be seen from the table, the reaction proceeds smoothly in the absence of a solvent, *i.e.* under conditions which are commonly used for hydrosilylation reactions. The complexes not containing stabilising triphenylphosphine ligands are effective already at ambient temperature. On the other hand, the palladium phosphine complex, which was reported to be ineffective in hydrosilylation of the diene by trimethylsilane<sup>1</sup>, exhibited catalytic activity at a temperature above 95°C. As to the effect on the overall yields, the use of the solvent benzene in the reactions catalysed by palladium–benzotrile and  $\pi$ -allyl complexes was found to be advantageous only when these reactions were carried out at elevated temperatures. Substitution of benzene for tetrahydrofuran, *i.e.* the solvent of higher polarity and coordination ability resulted in all cases in a decrease of overall yields, similarly as in the reaction of trimethylsilane with 1,3-butadiene<sup>1</sup> catalysed by a Pd(0) complex. On the other hand, the greater polarity of the solvent showed a favourable influence on the selectivity of the reaction with respect to formation of 1/2 adducts. As follows from the results given in Table III, the ratio of the 1/1 to 1/2 adducts increases with increasing temperature. This trend is most pronounced with the reactions carried out without solvent. As can be expected, even at elevated temperatures formation of 1/1 adducts can be suppressed by a sufficient excess of the diene. The dependence of the yields of 1/1 and 1/2 adducts on the 1,3-butadiene to triethoxysilane molar ratio is graphically represented in Figs 1 and 2. Analogous dependence was observed also with the palladium benzotrile complex. The decrease of both the overall yields and the yields of both adducts at molar ratios less than 1 was found to be caused by partial reduction of palladium complexes to metallic palladium during the reaction. The effect of reaction temperature on forma-

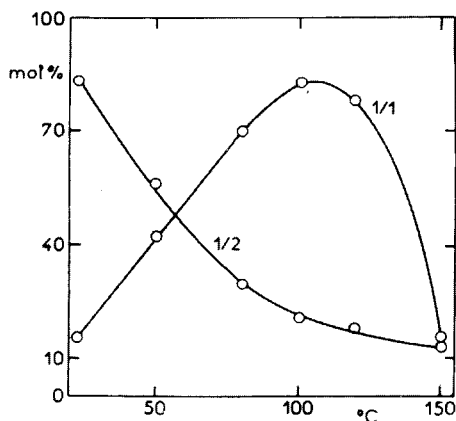


FIG. 3

Dependence of the Yields of 1/1 and 1/2 Adducts on Reaction Temperature for Reaction of Triethoxysilane with 1,3-Butadiene Catalysed by  $[\text{PdCl}(\pi\text{-C}_3\text{H}_5)_2]$  in the Absence of Solvent [Catalyst conc.  $2.75 \cdot 10^{-3}$  mol/mol  $(\text{C}_2\text{H}_5\text{O})_3\text{SiH}$ ],

○ 1/1 adducts, ● 1/2 adducts, the reactions were carried out over such a period of time which ensured that almost quantitative conversion of triethoxysilane was achieved. Molar yields of the products are calculated with respect to the silicon hydride.

tion of both adducts is shown in Fig. 3. The data in this figure were obtained under comparable, conditions for almost quantitative conversion of the silicon hydride in each case and at the butadiene to triethoxysilane ratio which ensured that the influence of side reactions leading to decomposition of the catalyst was minimised except the temperature 150°C where thermal decomposition could not be avoided. The palladium benzonitrile complex exhibited a similar behaviour. With dichloro-bis(triphenylphosphine)palladium(II) catalyst, the overall yield decreased with increasing temperature (in the 100–150°C temperature region), this being due to a decrease in the yields of both adducts. Again, the relative amount of 1/1 adducts increased with temperature (°C; overall yield, mol.%); the 1/1 to 1/2 adduct molar ratio: 100, 98, 1·8; 120, 72, 2·1; 150, 36, 3·5). Similar influence of reaction conditions was observed also in the reactions of the other members of the series, ethoxypropylsilane, diethoxypropyl-, propyldiethoxy-, and tripropylsilane (Table IV). With organosilicon hydrides substituted with bulky groups, the reaction produced selectively 1/2 adducts, except trineopentylsilane and tri(tert-butoxy)silane which did not react. Their yield was strongly influenced by reaction temperature. As shown in Table V, only moderate yields of 1/2 adducts were obtained at 100°C. The decrease in the yields of 1/2 adducts was not accompanied in this case by increased formation of 1/1 adducts. It can be thus attributed to the inactivation of catalysts, similarly as in the case of the triethoxysilane + 1,3-butadiene reaction. This is supported by the fact that trineopentylsilane, which did not add to 1,3-butadiene, reacted in the presence of this diene with  $\text{PdCl}_2[\text{P}(\text{C}_6\text{H}_5)_3]_2$  at 100°C to give metallic palladium.

It has recently been reported<sup>1</sup> that selective formation of the 1/1 adduct(s) in the reaction of trichlorosilane with 1,3-butadiene catalysed by a Pd(0) complex was due to thermal reactions. As follows from the results obtained in this study, this is not

TABLE IV

Hydrosilylation of 1,3-Butadiene by Diethoxypropyl-(A), Ethoxydipropyl-(B), and Tripropylsilane (C) Catalysed by  $[\text{PdCl}(\pi\text{-C}_3\text{H}_5)]_2$

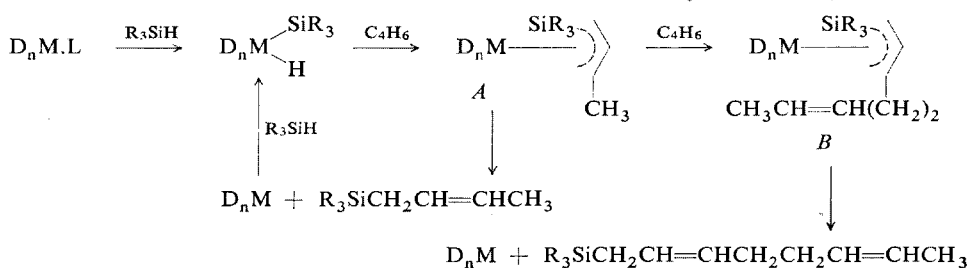
| °C/h <sup>a</sup><br>(solvent) | A, mol. % <sup>b</sup> |     | B, mol. % <sup>b</sup> |     | C, mol. % <sup>b</sup> |     |
|--------------------------------|------------------------|-----|------------------------|-----|------------------------|-----|
|                                | 1/1                    | 1/2 | 1/1                    | 1/2 | 1/1                    | 1/2 |
| 22/24 (—)                      | 4                      | 92  | 3                      | 96  | 0                      | 90  |
| 22/24 (B)                      | 4                      | 92  | 4                      | 95  | 0                      | 92  |
| 100/4 (—)                      | 38                     | 20  | 33                     | 10  | 2                      | 12  |
| 100/4 (B)                      | 39                     | 27  | 30                     | 13  | 1                      | 18  |

<sup>a</sup> For the other conditions see Table III. <sup>b</sup> The molar yields of the adducts calculated with respect to 1,3-butadiene.



the case with hydrosilylation reactions discussed above. In no case could the increase in the amounts of 1/1 adducts with increasing temperature have been ascribed to thermal additions occurring without participation of a catalyst. In fact, no addition of the organosilicon hydrides to the diene did occur at temperatures to 180°C. Formation of 1/1 adducts cannot also be due to the presence of metallic palladium formed during some of the reactions (especially at elevated temperatures) since it was found to be inactive.

We believe that the changes in relative amounts of both adducts in dependence on reaction conditions can be explained in terms of the mechanism postulated by Takahashi and coworkers<sup>1</sup> (Scheme 1), providing that increasing temperature,



D = donors

M = Pd, Ni

SCHEME 1

decreasing molar ratio of butadiene to organosilicon hydride, and the absence of donor ligands destabilize the  $\pi$ -allylic intermediate *A*. As the result, this intermediate decomposes to the products at a faster rate than it coordinates additional molecule of the diene to give the intermediate *B*. As can be expected, the ratio of 1/1 to 1/2 adducts depends also on the structure of the reactant silicon hydride. This effect is, however, weak (compare results in Tables III–V). The selectivity of the reaction, with respect to formation of 1/2 adducts, mildly increases with organosilicon hydrides substituted with electron-releasing and/or bulky groups. This inexpressive dependence might indicate that energy difference between the paths leading to 1/1 adduct and to 1/2 adduct is only slightly influenced by the nature of the silyl group. In order to examine the effect of the structure of silicon hydrides on their reactivity, we carried out hydrosilylation with the series of ethoxypropylsilanes under the conditions under which possible influence of other factors, such as side reactions, catalyst decomposition *etc.*, was insignificant (compare the yields obtained after 24 h, Table VI). As can be seen from Table VI, the reactivity, expressed by the overall yield obtained after 4h-reaction time, increases from tripropylsilane to ethoxydipropylsilane and then decreases. This trend does not follow strictly changes in the polarity of the Si—H bond of these compounds<sup>7</sup>. It is worthy of note that a similar dependence was also

observed for the chloroplatinic acid catalysed hydrosilylation of alkenes by the same series of silicon hydrides<sup>15,16</sup> and for base catalysed solvolysis of these compounds<sup>7</sup>. It was ascribed to the difference in steric demands of both groups when these are bonded to silicon. While the Si—C—C bond angle is 109°C, the Si—O—C bond angle may be increased due to back donation of free electron pairs of the oxygen to vacant silicon 3*d* orbitals. It seems likely that this factor is one of the reasons of the dependence found in this study.

TABLE V

The Yields of 1/2 Adducts Obtained by Hydrosilylation of 1,3-Butadiene by *tert*-Butoxydimethyl-(A), Di-*tert*-butoxymethyl-(B), Dimethylneopentyl-(C), and Methylneopentylsilane(D)

| Catalyst   | °C/h <sup>a</sup><br>(solvent) | 1/2 Adduct, mol. % <sup>b</sup> |    |    |    |
|--|--------------------------------|---------------------------------|----|----|----|
|  |                                | A                               | B  | C  | D  |
| [PdCl( $\pi$ -C <sub>3</sub> H <sub>5</sub> )] <sub>2</sub>                      | 22/24 (—)                      | 98                              | 99 | 96 | 97 |
|  | 22/24 (B)                      | 97                              | 98 | 97 | 96 |
|  | 100/4 (—)                      | 17                              | 17 | 33 | 15 |
|  | 100/4 (B)                      | 21                              | 20 | 28 | 9  |
| PdCl <sub>2</sub> [P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>2</sub> | 100/4 (—)                      | 31                              | 35 | 77 | 63 |
|  | 100/4 (B)                      | 28                              | 11 | 38 | 47 |

<sup>a</sup> For the other conditions see Table III. <sup>b</sup> The molar yields of the adducts calculated with respect to 1,3-butadiene.

TABLE VI

Comparison of Overall Yields (mol. % with respect to 1,3-Butadiene) for Hydrosilylation of 1,3-Butadiene by the Ethoxypropylsilanes (C<sub>2</sub>H<sub>5</sub>O)<sub>3-n</sub>(n-C<sub>3</sub>H<sub>7</sub>)<sub>n</sub>SiH (*n* = 0–3) Catalysed by [PdCl( $\pi$ -C<sub>3</sub>H<sub>5</sub>)]<sub>2</sub> at 22°C

Catalyst conc.  $2.75 \cdot 10^{-3}$  mol/mol R<sub>3</sub>SiH, the 1,3-C<sub>4</sub>H<sub>6</sub> : R<sub>3</sub>SiH mol. ratio = 1.8 : 1, 0.4 ml benzene/mmol R<sub>3</sub>SiH.

| R <sub>3</sub> SiH   | The overall yield after |      | 1/1 to 1/2 Adducts |      |
|--|-------------------------|------|--------------------|------|
|  | 4 h                     | 24 h | 4 h                | 24 h |
| (n-C <sub>3</sub> H <sub>7</sub> ) <sub>3</sub> SiH                                  | 19                      | 92   | 0                  | 0    |
| C <sub>2</sub> H <sub>5</sub> O(n-C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> SiH   | 82                      | 97   | 0.07               | 0.10 |
| (C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> (n-C <sub>3</sub> H <sub>7</sub> )SiH | 77                      | 96   | 0.07               | 0.10 |
| (C <sub>2</sub> H <sub>5</sub> O) <sub>3</sub> SiH                                   | 61                      | 99   | 0.11               | 0.10 |

TABLE VII

The Ratio of 1-Silylsubstituted *cis*- to *trans*-2-Butenes Obtained by Hydrosilylation of 1,3-Butadiene by Triethoxysilane in Dependence on Reaction Temperature and Catalyst  
For conditions see Table III.

| Catalyst   | The <i>trans</i> : <i>cis</i> ratio |            |
|--|-------------------------------------|------------|
|  | 22°C, 24 h                          | 100°C, 4 h |
| PdCl <sub>2</sub> (C <sub>6</sub> H <sub>5</sub> CN) <sub>2</sub>                | 3·2                                 | 2·1        |
| [PdCl(π-C <sub>3</sub> H <sub>5</sub> ) <sub>2</sub> ] <sub>2</sub>              | 3·1                                 | 2·3        |
| PdCl <sub>2</sub> [P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>2</sub> | — <sup>a</sup>                      | 0·1        |

<sup>a</sup> The catalyst was inactive.

The 1/2 adducts formed by the addition of all the silicon hydrides studied were found by IR and NMR spectroscopy to be 1-silyl-2,6-octadienes (Tables I and II), in harmony with the assumption that the reaction proceeds *via* the π-allylic intermediate *B* depicted in Scheme 1. The mechanism suggested by Takahashi and coworkers<sup>1</sup> further implies that 1/1 adducts should have the structure of terminal silylsubstituted 2-butenes. As found in the present work, this was the case with triethoxysilane. Its addition to 1,3-butadiene produced a mixture of 1-triethoxysilyl-*cis*- and -*trans*-2-butenes, the ratio of these isomers being dependent on reaction temperature and catalyst (Table VII). We have further confirmed that the *trans* isomer is not produced by consecutive isomerisation of the *cis* isomer. This indicates that this compound is formed directly from the intermediate *A* (*i.e.* during product formation step and not *via* subsequent coordination of the *cis* isomer to the metal). On the contrary, the additions of diethoxypropyl- and ethoxydipropylsilanes gave unexpectedly terminal silylsubstituted 1-butenes, 1-diethoxypropylsilyl-1-butene and 1-ethoxydipropylsilyl-1-butene, along with corresponding silylsubstituted 1,3-butadienes. Formation of these substances clearly demonstrates that the mechanism of the reaction under study is more complex than it is depicted in Scheme 1. This problem will be discussed in a subsequent paper.

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