# HYDROSILYLATION OF 1,3-BUTADIENE WITH ALKYL- AND ALKOXYSILANES CATALYSED WITH Ni(II) AND Ni(0) COMPOUNDS*

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The addition of alkylsilanes $R_3SiH$ (R = $CH_3$, $C_2H_5$, n-$C_3H_7$) and alkoxysilanes $(C_2H_5O)_{3-n}$.$(n$-$C_3H_7)_nSiH(n = 0-2)$ to 1,3-butadiene catalysed with bis(1,5-cyclooctadiene)nickel, $NiX_2$ and $NiX_2$–L systems (X = F, Cl, Br, I, $CH_3CH(OH)COO$, $CH_3C(-O)=CHCH(=O)CH_3$; L=$P(C_6H_5)_3$, $P(n$-$C_4H_9)_3$, $P(C_6H_{11})_3$, $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2)$ was studied. The reaction produced 1-silyl-substituted *cis*-2-butenes as main products which were accompanied by small amounts of 1-silyl-substituted 2,6-octadienes. In contrast to the hydrosilylation catalysed with palladium complexes, relative amounts of the silyl-substituted butenes and octadienes formed were only slightly affected by temperature, solvent and the butadiene to silicon hydride ratio. Similar selectivities achieved for individual organosilicon hydrides with both nickel(II) and nickel(0) compounds indicate that the reactions proceed *via* common reaction intermediate.

In recent years, increasing attention has been paid to nickel compounds as catalysts for hydrosilylation of alkenes[1−6] and alkadienes[7−10]. In our previous work[10] we were concerned with the Ni(II) and Ni(O)-catalysed addition of trichlorosilane to 1,3-butadiene. The reaction produced trichlorosilylbutenes as main products which in some cases were accompanied by small amounts of the bis-trichlorosilyl derivatives. The adducts of trichlorosilane to two butadiene molecules, silyl-substituted octadienes, have not been formed, in contrast to the addition of trimethylsilane catalysed with nickel(0) complexes (nickel(II) compounds were ineffective)[7] which yielded 1-trimethylsilyl-2-butene and 1-trimethylsilyl-2,6-octadiene (formed in nearly tenfold excess with respect to the butene). In the latter case also the butadiene cyclodimer, 1,5-octadiene, was found among reaction products in relatively great amounts (20 per cent). A similar nickel-catalysed addition of alkoxysilanes has not up to now been studied. With alkyl- or alkoxysilanes and palladium(II) compounds as catalysts[11,12], the above cyclodimer was formed in amounts less than 3 per cent. The reaction gave 1-silyl-substituted 2,6-octadienes (1 : 2 adducts) and 1-silyl-substituted butenes (1 : 1 adducts), the former being major products. Relative amounts of 1 : 2

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and 1 : 1 adducts were, however, strongly affected by reaction temperature, solvent and by the butadiene to organosilicon hydride ratio.

The diversity of reaction products and their dependence on the above factors led us to examine nickel-catalysed hydrosilylation of 1,3-butadiene with alkyl- and alkoxysilanes. The aim of the present work was to ascertain how replacement of palladium by the smaller nickel atom having higher $d_\pi$ acceptor ability[13,14] affects the selectivity of the reaction. We were also interested in using readily available nickel(II) compounds in place of the thus far employed nickel(0) complexes[7] or Ziegler systems[8,9] as catalysts for this reaction.

## EXPERIMENTAL

Purity of all the compounds was verified by gas chromatography, index of refraction or melting point determination (Kofler microscope). All operations with hydrolysable or air-sensitive compounds were carried out under an atmosphere of nitrogen.

*Compounds used.* 1,3-Butadiene (>98%, Kaučuk, Kralupy n/Vlt.) was used in liquid state dried over a molecular sieve. Trichlorosilane and methyldichlorosilane (VCHZ Synthesia, Kolín) were purified by distillation through a 20 TP column. Trimethylsilane[15], triethylsilane[16], tripropylsilane[17], ethoxydipropylsilane[18], diethoxypropylsilane[18], and triethoxysilane[18] were prepared by reported procedures. Nickel compounds and tertiary phosphines were of the same provenience as in a previous work[10].

*Hydrosilylation.* All experiments were carried out under argon with degassed reactants and solvents in sealed tubes which were placed in a thermostated bath and agitated. Until analysed, the samples were stored at a temperature of $-78°C$. Experimental conditions are given in Tables *I—IV*, the procedure and chromatographic analysis were described in detail elsewhere[11].

*Hydrosilylation products.* The following products of the hydrosilylation of 1,3-butadiene were reported in our previous works and the products formed were therefore identified by their comparing with these authentic samples by means of gas chromatography and IR spectroscopy; 1-trichlorosilyl-*cis*-2-butene[19], 1,4-bis(trichlorosilyl)-2-butene[10], 1-trimethylsilyl-2,6-octadiene[12], 1-tripropylsilyl-2,6-octadiene[11], 1-ethoxydipropylsilyl-2,6-octadiene[11], 1-diethoxypropylsilyl-2,6--octadiene[11], and 1-triethoxysilyl-2,6-octadiene[11]. 1-Triethylsilyl-2,6-octadiene was prepared by procedure reported by Tsuji and coworkers[20]. In contrast to the palladium-catalysed addition of triethoxysilane to 1,3-butadiene[11], the nickel-catalysed one produced three isomeric triethoxysilyloctadienes, as shown by combined gas chromatographic–mass spectrometric analysis. The position of the silyl group and the double bonds in these isomers is uncertain, since they were formed in amounts which were insufficient for more detailed structural analysis. The other products were isolated from reaction mixtures by fractional distillation or by preparative gas chromatography. These were characterized by IR spectra (Table V) and showed satisfactory elemental analyses. 1-Trialkylsilyl-*cis*-2-butenes were also prepared by alkylation of 1-trichlorosilyl-*cis*-2-butene with alkylmagnesium bromide. In a typical example, 4 ml (26 mmol) of 1-trichlorosilyl-*cis*-2-butene dissolved in 10 ml of diethyl ether were slowly added to 100 ml of 1M ether solution of alkylmagnesium bromide. The mixture was kept under reflux for 4 h, acidified by dilute HCl at 0°C and worked-up in the usual way. Distillation afforded corresponding 1-trialkylsilyl-*cis*-2-butenes in 50 to 70% yields. 1,4-Bis(trimethylsilyl)-2-butene was prepared similarly from the corresponding trichlorosilyl derivative[10]. 1-Triethoxysilyl-*cis*-2-butene was prepared in the following way: a solution of 26 mmol (4 ml) of the trichlorosilyl derivative in 20 ml of di-

ethyl ether was added dropwise with stirring to a mixture of 5·25 ml (90 mmol) of ethanol and 7·2 ml (90 mmol) of pyridine. The mixture was refluxed for 2 h and cooled to room temperature, the precipitate pyridine hydrochloride was filtered off and the liquid layer distilled to give the product in 62% yield.

*Spectroscopic measurements.* IR spectra in the $4000-400 \text{ cm}^{-1}$ region were recorded on a double-beam Zeiss spectrophotometer, Model UR-20 (Jena, GDR) using the compounds as capillary layers between KBr plates or as 5% solutions in $CCl_4$ or $CS_2$ (0·008 cm cells). Mass spectra were measured with a Gas chromatograph–mass spectrometer, type LKB 9000 (70 eV ionizing energy of electrons).

## RESULTS AND DISCUSSION

In the presence of nickel or palladium compounds[7-12] 1,3-butadiene reacts with organosilicon hydrides to give silyl-substituted butenes and octadienes as main

TABLE I

Addition of Organosilicon Hydrides (8·6 mmol) to 1,3-Butadiene (12 mmol) Catalysed with Bis(1,5-cyclooctadiene)nickel (0·03 mmol) in Benzene (2 ml)
Reaction time 1·5 h, temperature 80 and 120°C (data in parentheses).

| $R_3SiH$ | Yield, %[a] | | $BD^b$ | $BT^c$ | $II/I$ mol. ratio |
|---|---|---|---|---|---|
| | $I$ | $II$ | | | |
| $Cl_3SiH$ | $76^d$ | 0 | 0 | 0 | 0 |
| | $(73)^d$ | $(3)^e$ | (0) | (0) | (0·04) |
| $Cl_2CH_3SiH$ | 93 | $6^e$ | 0 | 0 | 0·07 |
| | (93) | $(7)^e$ | (0) | (0) | (0·08) |
| $(CH_3)_3SiH$ | 51 | 8 | 1 | 0 | 0·16 |
| | (80) | (12) | (1) | (0) | (0·15) |
| $(C_2H_5)_3SiH$ | 65 | 23 | 0 | 5 | 0·35 |
| | (70) | (26) | (0) | (8) | (0·37) |
| $(n\text{-}C_3H_7)_3SiH$ | 52 | 24 | 0 | 1 | 0·46 |
| | (61) | (30) | (0) | (7) | (0·49) |
| $(C_2H_5O)(n\text{-}C_3H_7)_2SiH$ | 67 | 8 | 0 | —$^f$ | 0·12 |
| | (85) | (10) | (0) | (7) | (0·12) |
| $(C_2H_5O)_2(n\text{-}C_3H_7)SiH$ | 75 | 6 | 0 | 2 | 0·08 |
| | (87) | (8) | (2) | (8) | (0·09) |
| $(C_2H_5O)_3SiH$ | 93 | $6^g$ | —$^f$ | 2 | 0·06 |
| | (92) | $(7)^g$ | (2) | (5) | (0·08) |

[a] With respect to the silicon hydride; $I$ $R_3SiCH_2CH{=}CHCH_3$ (*cis*); $II$ $R_3SiCH_2CH_2{=}CH(CH_2)_2$.
.$CH{=}CHCH_3$. [b] Butadiene dimers in per cent by weight determined by gas chromatographic analysis of the reaction mixture freed of components boiling below 10°C. [c] Butadiene trimers in per cent by weight (see footnote[b]). [d] $Cl_3SiCH_2CH_2CH{=}CH_2$ was also formed in 22% yield. [e] The yield of $R_3SiCH_2CH{=}CH_2CH_2SiR_3$. [f] Trace amounts. [g] Three isomers.

products. Preliminary experiments showed that in contrast to the palladium-catalysed hydrosilylation[11], the nickel-catalysed addition of alkyl- and alkoxysilanes studied gave corresponding silyl-substituted butenes (1 : 1 adducts) as major products. The structure of these compounds was elucidated on the basis of their IR spectra.

TABLE II

Effect of Solvents (2 ml) on Addition of Triethoxy- and Triethylsilane (9·6 mmol) to 1,3-Butadiene (12 mmol) Catalysed with Bis(1,5-cyclooctadiene)nickel (0·03 mmol) at 80°C (1·5 h)

| Solvent | Yield, %[a,b] | | | $IIa/Ia$ mol. ratio | Yield, %[a,c] | | | $IIb/Ib$ mol. ratio |
|---|---|---|---|---|---|---|---|---|
| | $Ia$ | $IIa$ | $BT^d$ | | $Ib$ | $IIb$ | $BT^d$ | |
| None | 94 | 5 | 1 | 0·05 | 66 | 22 | 5 | 0·33 |
| $C_6H_6$ | 96 | 4 | 4 | 0·04 | 52 | 15 | 6 | 0·29 |
| n-$C_7H_{16}$ | 96 | 4 | 3 | 0·04 | 63 | 20 | 6 | 0·32 |
| THF[e] | 95 | 5 | 3 | 0·05 | 7 | 2 | 1 | 0·29 |
| HMPT[f] | 88 | 6 | 0 | 0·07 | 23 | 7 | 0 | 0·30 |

[a] With respect to the silicon hydride. [b] $Ia$ 1-Triethoxysilyl-*cis*-2-butene, $IIa$ a mixture of isomeric triethoxysilyloctadienes. [c] $Ib$ 1-Triethylsilyl-*cis*-2-butene, $IIb$ 1-triethylsilyl-2,6-octadiene. [d] Butadiene trimers in per cent by weight (see footnote[b] to Table I). [e] Tetrahydrofuran. [f] Hexamethylphosphorous triamide, reaction temperature 120°C.

TABLE III

Yield (mol.%) of 1-Triethoxysilyl-*cis*-2-butene (*Ia*) and Triethoxysilyloctadienes (*IIa*) Obtained by Hydrosilylation of 1,3-Butadiene (32 mmol) with Triethoxysilane (26 mmol) Catalysed with a Nickel(II) Salt (0·04 mmol)–Tertiary Phosphine (0·2 mmol) System (120°C, 3 h)

| Ni(II) compound[a] | None | | $P(C_6H_5)_3$ | | | $P(n-C_4H_9)_3$ | |
|---|---|---|---|---|---|---|---|
| | $Ia$ | $IIa$ | $Ia$ | $IIa$ | $COD^b$ | $Ia$ | $IIa$ |
| $NiF_2$ | 28 | 0 | 77 | 1 | 5 | 2 | c |
| $NiCl_2$ | 61 | 4 | 70 | 6 | 5 | 2 | 0 |
| $NiBr_2$ | 28 | 0 | 54 | 4 | 6 | 1 | 0 |
| $NiI_2$ | —[c] | 0 | 60 | 5 | 11 | 5 | 1 |
| [Ni(acac)$_2$][d] | 92 | 5 | 61 | 5 | 8 | 5 | 0 |
| $Ni(C_3H_5O_3)_2$[e] | 69 | 6 | 76 | 2 | 5 | 90 | 2[f] |

[a] Yields were calculated with respect to the silicon hydride. [b] 1,5-Cyclooctadiene in per cent by weight (*cf.* footnote[b] to Table I). [c] Traces. [d] acac = acetylacetonyl. [e] $C_3H_5O_3 = CH_3CH(OH)COO^{(-)}$. [f] Also 1% COD.

The products of 1,2- and 1,4-addition, 1-silyl-substituted butenes can be readily distinquished by their IR absorptions above $3000\ cm^{-1}$ (the $=C—H$ stretching vibration): the internal $—CH=CH—$ double bond is characterized by one band $(3030-3020\ cm^{-1})$ while the terminal $—CH=CH_2$ group by the two absorption bands $(3030-3020\ and\ 3080\ cm^{-1})$. All the 1 : 1 adducts obtained showed one absorption band (liquid films, Table V) and were assigned the structure of 1-silyl--substituted 2-butenes. Their configuration (*cis, trans*) was deduced from the following facts. Each isomer is characterized[21] by one absorption band which occurs at around $700\ cm^{-1}$ for the *cis* isomer and at around $960\ cm^{-1}$ for the *trans* isomer. There are, however, cases where some groups or bonds in the molecule can interfere in the above regions. With the compounds under study these are the stretching vibrations of $SiC_2$ and $SiC_4$ arrangements that absorb in the $800-650\ cm^{-1}$ and mask the band characteristic for the *cis* configuration. Another interference is due to the C—C stretching vibration of the ethyl substituent in the triethylsilyl or triethoxysilyl groups that occurs at $960\ cm^{-1}$ and might be erroneously interpreted as being evidence for the *trans* configuration of the 1,2-disubstituted C=C bond. In both cases indirect informations from other regions of the spectrum concerning intensities of the bands or occurrence of new bands are useful, as proved in the case of 1-trichlorosilyl-2-butenes[22]. One of them is a medium band of the $v(C=C)$ near $1650\ cm^{-1}$ for the *cis* isomer, while the corresponding band for the *trans* isomer is weak or missing due to pseudocenter of symmetry of the molecule. The results show that 1-silyl-substituted 2-butenes presented in Table V all are the *cis* isomers. This assignment is supported also by the following facts. 1-Trimethylsilyl-, 1-triethylsilyl-, and 1-tri-n-propylsilyl-2-butenes prepared by alkylation of 1-trichlorosilyl-*cis*-2-butene showed identical pattern of the IR spectra in the $1000-900\ cm^{-1}$ region and the same gas chromatographic retention times on capillary column as the compounds isolated from the reaction mixture (Table V). Further, 1-trimethylsilyl-*cis*-2-butene obtained by methylation of 1-dichloromethylsilyl-*cis*-2-butene was identical with the product of the alkylation of 1-trichlorosilyl-*cis*-2-butene. Also 1-triethoxysilyl-2-butene obtained from the reaction mixture and prepared by esterification of the trichlorosilyl derivative were identical. In no case formation of the isomers having the silyl group attached to the carbon atom in position 2 of the chain has been established, in contrast to the addition of triethoxysilane to 1,3-pentadiene catalysed with Ziegler systems[9].

The results obtained in the reaction of organosilicon hydrides with 1,3-butadiene catalysed with bis (1,5-cyclooctadiene)nickel are presented in Table I. Their comparison with the related palladium-catalysed hydrosilylation[7,11,12] reveals several specific features of the reaction under study. With the exception of trichlorosilane, and to a lesser extent also dichloromethylsilane (the factors controlling the addition of the former compound were discussed elsewhere[10]), in the presence of the nickel complex the structure of the silyl-substituted butenes formed does not essentially

depend on the reactant silicon hydride. Although with all the alkyl- and alkoxysilanes but triethoxysilane the only 1 : 2 adduct formed is 1-silyl-substituted 2,6-octadiene, its formation is substantially suppressed compared to the palladium-catalysed addition. The ratio of the 1 : 1 to 1 : 2 adducts depends only slightly on the reactant. The results indicate that the distribution of the products is controlled mainly by electronegativity of substituents at silicon and less by steric effects (compare the results for triethyl- and tripropylsilane with those for diethoxypropyl- and triethoxysilane). It is remarkable that the distribution of the products is not essentialy affected by change of reaction temperature (see results for 80 and 120°C), again in contrast to the palladium-catalysed addition. In harmony with this are also the solvent effects observed. In spite of the fact that only two solvents were investigated in the latter case (benzene, tetrahydrofuran)[11] it became evident that the more polar and coordinating solvent preferred formation of 1 : 2 adducts in the expense of activity of the catalytic system.

TABLE IV

Effect of the Butadiene to Triethoxysilane Ratio on Distribution of Hydrosilylation Products For reaction conditions see Table III.

| Ni compound | 1,3-$C_4H_6$ mmol | Yield, %[a] | | |
| --- | --- | --- | --- | --- |
| | | Ia | IIa | COD[b] |
| [Ni(COD)$_2$] | 8 | 29 (94) | 2 (4) | 2 |
| | 15 | 53 (92) | 4 (7) | 2 |
| | 31 | 86 | 4 | 5 |
| | 62 | 85 | 9 | 4 |
| Ni($C_3H_5O_3$)$_2$[c] + P($C_6H_5$)$_3$ | 8 | 27 (89) | 0 | 0 |
| | 15 | 45 (78) | 1 (2) | 1 |
| | 31 | 77 | 2 | 4 |
| | 62 | 80 | 8 | 15 |
| | 124 | 74 | 10 | 31 |
| [Ni(acac)$_2$][d] + P($C_6H_5$)$_3$ | 8 | 29 (94) | 1 (3) | 1 |
| | 15 | 48 (83) | 3 (5) | 5 |
| | 31 | 60 | 5 | 8 |
| | 62 | 47 | 5 | 19 |
| | 124 | 52 | 5 | 47 |

[a] Determined by gas chromatography. Data in parentheses represent conversions calculated with respect to the amount of the silicon hydride which could theoretically react due to substoichiometric amount of 1,3-butadiene. [b] COD 1,5-cyclooctadiene in per cent by weight determined and calculated similarly as described in footnote[b] to Table I. [c] See footnote[e] to Table III. [d] See footnote[d] to Table III.

$$M = Pd, Ni$$
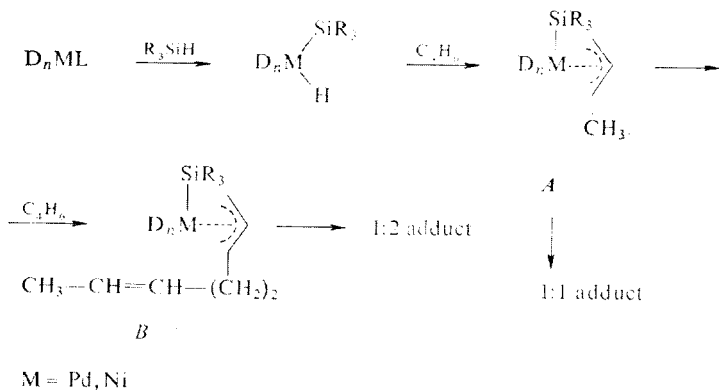
SCHEME 1

On the other hand (Table II), the selectivity of the nickel-catalysed reaction was not essentially affected even by using such highly polar solvent as hexamethylphosphor triamide. In that case, however, the nickel complex was inefficient at 80°C and reasonable yields of hydrosilylation products were obtained at substantially higher temperature compared to the other solvents.

It has been proposed[7] that both palladium- and nickel-catalysed hydrosilylation of 1,3-butadiene proceed *via* identical reaction mechanism involving formation of π-allyl intermediates $A$ and $B$ (Scheme 1). Differences between both reactions discussed above do not contradict this assumption. The preferential formation of 1 : 1 adducts in the hydrosilylation catalysed with bis(1,5-cyclooctadiene) nickel only shows that in this case the intermediate $A$ is converted to products at faster rate than it is transformed to the intermediate $B$. The smaller atomic radius of nickel



$$M = Pd, Ni$$
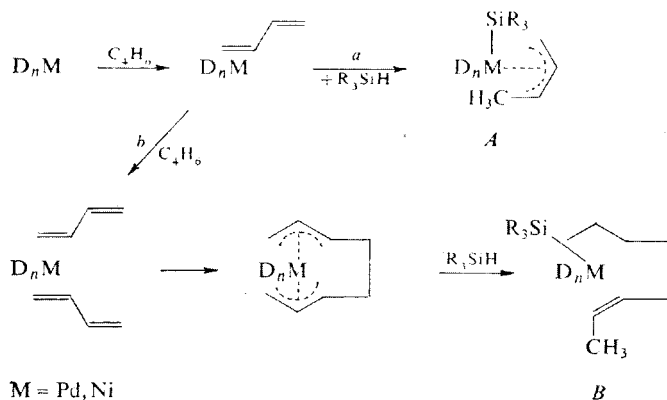
SCHEME 2

compared to palladium and consequent increasing steric screening by lingads may significantly contribute to this fact. Highly selective formation of 1 : 1 adducts (exclusively the *cis* isomers) further indicates that the methyl group in π-allyl intermediate *A* occupies the *syn*-position (Scheme 2).

It should be mentioned that the mechanism depicted in Scheme 1 is not the only one which would be in accordance with the thus far reported results, since intermediates *A* and *B* may in principle arise also *via* precoordination of butadiene molecule. This route visualized in Scheme 2 is closely related to cyclooligomerization mechanism suggested by Wilke and coworkers[23,24] and could explaine why addition reaction is accompanied by formation of butadiene dimers and trimers. The dependence of the distribution of the reaction products (1 : 1 and 1 : 2 adducts) on the structure of organosilicon hydrides (Table I) can be then ascribed to increasing importance of path *a*) relative to path *b*) with increasing electronegativity and number of substituents at silicon. At present there are no data allowing to distinguish between these alternatives.

With regard to possible technical importance of triethoxysilylbutenes we were also concerned with synthetic aspects of the addition. We have recently found[10] that the addition of trichlorosilane to 1,3-butadiene can be effected in the presence of nickel(II) complexes. We find now that the addition of triethoxysilane can not only be catalysed with *in situ* formed nickel compounds of the type $[NiX_2L_2]$ (X = anionic ligand, L = neutral ligand) but contrary to the previous case[10] also with simple salts of divalent nickel. The results presented in Table III show that in the absence of a tertiary phosphine, the activity of nickel salt depends on the acid

TABLE V
IR Spectra of Silyl-Substituted *cis*-2-Butenes $R_3SiCH_2CH{=}CHCH_3$ (cm$^{-1}$)
Symbols used: w weak, m medium, s strong, br broad.

| $SiR_3$ | Band near 700 cm$^{-1}$ | Additional bands | | | $\nu(C{=}C)$ |
|---|---|---|---|---|---|
| $SiCl_3$ | 677 m | 902 m | 961 w | 991 s | 1 653 m |
| $SiCl_2CH_3$ | 660 m | 910 br | 968 w | 992 m | 1 651 m |
| $Si(CH_3)_3$ | —[a] | 901 m | 865 w | 991 s | 1 651 m |
| $Si(C_2H_5)_3$ | —[a] | 990 w | 970 br | 992 m | 1 650 m |
| $Si(n\text{-}C_3H_7)_3$ | —[a] | 899 m | 950 w | 995 br, s | 1 650 m |
| $Si(OC_2H_5)(n\text{-}C_3H_7)_2$ | —[b] | 898 m | 948 s[c] | 996 s | 1 651 m |
| $Si(OC_2H_5)_2(n\text{-}C_3H_7)$ | —[d] | 900 w | 954 s[e] | 995 m | 1 651 m |
| $Si(OC_2H_5)_3$ | 705 m | 905 w | 961 s[f] | 994 m | 1 651 m |

[a] Masked by $\nu(SiC_4)$. [b] Masked by $\nu(SiC_3)$. [c] One ethoxy group. [d] Masked by $\nu(SiC_2)$. [e] Two ethoxy groups. [f] Three ethoxy groups.

anion. The addition produces again 1 : 1 adducts as major products. In the presence of tertiary phosphines these differences are suppressed. With the exception of nickel lactate, the addition of more basic tributylphosphine markedly reduces the yields of hydrosilylation products, in the presence of tricyclohexylphosphine or 1,2-bis-(diphenylphosphine)ethane even this nickel salt is essentially ineffective.

Similarity in the course of the addition catalysed with nickel(II) and nickel(O) compounds is further demonstrated by the results concerning the effect of the butadiene to triethoxysilane ratio (Table IV). Small change in the selectivity of the reaction due to variance in relative amounts of the reactants is in harmony with similarly small effects of reaction temperature and solvent and is an additional feature by which the nickel-catalysed addition differs from the palladium-catalysed one[11,12].

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