STERIC EFFECTS IN HYDROSILYLATION OF STYRENE*

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Hydrosilylation of styrene, 2-phenyl-1-propene, *trans*-1-phenyl-1-propene by $(CH_3)R_2SiH$ ($R = C_2H_5$, i-C_3H_7, i-C_4H_9) and R'_3SiH ($R' =$ i-C_3H_7, t-C_4H_9) in the presence of $[RhCl.\{P(C_6H_5)_3\}_3]$ (*I*), $[\{RhCl(C_2H_4)_2\}_2]$ (*II*) and H_2PtCl_6 as catalysts has been studied. The reaction of styrene with $(CH_3)R_2SiH$ catalysed by complex *I* in benzene leads to α- and β-adduct as well as to a substitution product. Analogous addition of (i-$C_3H_7)_3SiH$ catalysed by complexes *I* and *II* produces selectively *trans*-1-triisopropylsilyl-2-phenylethylene. Reaction of 2-phenyl-1-propene with $CH_3(C_2H_5)_2SiH$ gives 1-diethylmethylsilyl-2-phenylpropane, 1-diethylmethylsilyl-2-phenyl-2-propene and 1-diethylmethylsilyl-2-phenyl-1-propene. Hydrosilylation of *trans*-1-phenyl-1-propene by diethylmethylsilane catalysed by complex *I* gave 1-diethylmethylsilyl-2-phenylpropane and 3-diethylmethylsilyl-1-phenylpropane. Conversion of 2-phenyl-1-propene and *trans*-1-phenyl-1-propene in their reaction with diethylmethylsilane catalysed by complex *I* was found to be much lower compared to the reaction with styrene and attained maximum at 60°C. The selectivity and rates of above reactions can be influenced by the presence of air oxygen.

Selectivity of the reaction of styrene with organosilicon hydrides homogeneously catalysed by Group VIII transition metal complexes has been investigated by a number of authors[1-12]. Selective catalysts for preparing α- and β-adducts have been reported[1,2] and the effect of the addition of coordinating compounds on isomer distribution has been examined[1,3]. When studying this addition catalysed by H_2PtCl_6 (refs[4,5]) and $[RhCl\{P(C_6H_5)_3\}_3]$ (*I*) (ref.[6]) the authors found that organosilicon hydride is playing a decisive role in determining adducts distribution. However, to which extent is this ratio influenced by steric or electronic effects of substituents of organosilicon hydride has not yet been determined. Reported data do not allow to ascertain whether the higher rate of hydrosilylation in the presence of oxygen is due to steric effects, shift in triphenylphosphine dissociation from complex *I* to form $[RhCl\{P(C_6H_5)_3\}]$ *via* oxidation of triphenylphosphine or due to electronic changes caused by oxygen-containing ligand in the coordination sphere of the metal. The aim of this work was to contribute to the elucidation of these problems.

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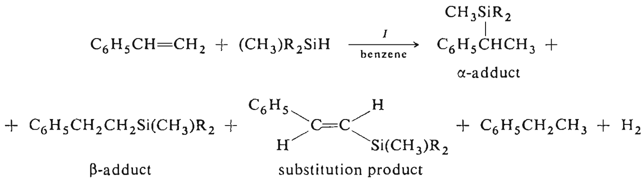
RESULTS AND DISCUSSION

We found that styrene reacts with trialkylsilicon hydrides of the type $(CH_3)R_2SiH$ in the presence of complex *I* in benzene to form three organosilicon products, ethylbenzene and hydrogen (*A*)



(*A*)

Branching of the alkyl group attached to the silicon atom of organosilicon hydride affects substantially the yield and composition of organosilicon products and shifts the distribution in favour of the β-adduct and substitution product (Table I). Distance between the branching and the silicon atom determined the ratio of hydrosilylation to substitution products. If a given alkyl group is branched on the β-carbon atom with respect to silicon $(CH_3(i\text{-}C_4H_9)_2SiH)$ the β-adduct to substitution product ratio remains the same as in the reaction with trialkylsilicon hydride containing

TABLE I

The Effect of Branching of Alkyl Group Attached to Silicon on Reaction of Styrene with Trialkylsilanes Catalysed by Complex *I*

$I/C_6H_5CH{=}CH_2$ molar ratio = 10^{-4}, the catalyst added as $8{\cdot}7 \,.\, 10^{-4}$ mol/l benzene solution, 70°C, 6 h (equimolar amounts of reactants).

Silicon hydride	X, %[a]	Composition of organosilicon products, %		
		α-adduct	β-adduct	A[b]
$CH_3(C_2H_5)_2SiH$	98·0	29·1	56·9	14·0
$CH_3(i\text{-}C_4H_9)_2SiH$	97·0	12·5	69·1	18·4
$CH_3(i\text{-}C_3H_7)_2SiH$	93·0	1·7	27·8	70·5

[a] Conversion of styrene. [b] Substitution product (Eq. (*A*)). All hydrogen evolved by addition-elimination reaction reacted with styrene to form ethylbenzene.

unbranched alkyl groups ($CH_3(C_2H_5)_2SiH$). Branching of alkyl groups on the α-carbon leads to such sterical shielding that substitution products prevail over adducts, as found in the addition of diisopropylmethylsilane to styrene. Triisopropylsilane does not react with styrene in benzene solution. This reaction can be effected in the absence of the solvent (*I*/styrene molar ratio = 10^{-3}, 100°C). Increasing catalyst concentration increases styrene conversion (Table II). *trans*-1-Triisopropylsilyl-2-phenylethylene was found as a sole reaction product. Screening of the Si—H bond by three tert-butyl groups is probably the reason why $(t\text{-}C_4H_9)_3SiH$ does not react with styrene even under conditions under which styrene was converted quantitatively

TABLE II

The Effect of Catalyst Concentration on the Yield of *trans*-1-Triisopropylsilyl-2-phenylethylene
Styrene/$i\text{-}(C_3H_7)_3SiH$ molar ratio = 1, 100°C, 6 h.

I/styrene mol. ratio	X, %[a]	Y[b]
10^{-4}	0	0
10^{-3}	55·0	1·4
10^{-2}	100·0	1·25

[a] Conversion of styrene. [b] Y denotes the ratio of the substitution $C_6H_5CH{=}CH_2 + R_3SiH \rightarrow C_6H_5CH{=}CHSiR_3 + H_2$ to the hydrogenation $C_6H_5CH{=}CH_2 + H_2 \rightarrow C_6H_5CH_2CH_3$. At Y = 1 all the hydrogen evolved by the addition-elimination reaction was consumed by hydrogenation of styrene.

TABLE III

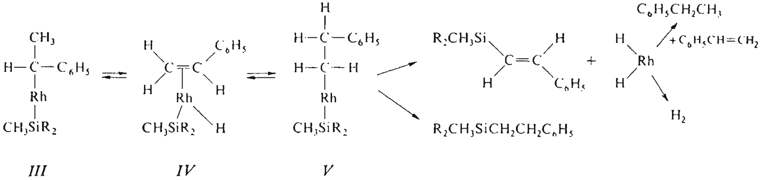
Conversion of Styrene (X) and Composition of Organosilicon Products in Reaction of Styrene with Trialkylsilanes
Styrene/R_3SiH molar ratio = 1, *I*/styrene molar ratio = $5 . 10^{-3}$, 100°C, 6 h.

Silicon hydride	X, %	Composition of organosilicon products, %		Y[a]
		β-adduct	A[a]	
$CH_3(C_2H_5)_2SiH$	100	69·3	20·7	1·23
$CH_3(i\text{-}C_3H_7)_2SiH$	100	0	100·0	1·25
$(i\text{-}C_3H_7)_3SiH$	62	0	100·0	1·41

[a] For designation see Table I.

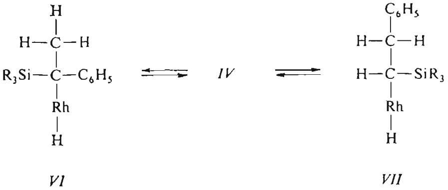
in its reaction with $(i\text{-}C_3H_7)_3SiH$. Using such high catalyst concentrations and carrying out the reaction in the absence of solvent, hydrosilylation of styrene by diethylmethylsilane does not yield the α-adduct (Table III). In this case the yield of the substitution product increases, along with an increase in the amount of hydrogen which is not utilized for hydrogenation of styrene.

These results can be explained in terms of the reaction mechanism proposed by Chalk and Harrod[13]. A decrease in the yield of α-adduct in the series $CH_3.(C_2H_5)_2SiH$, $CH_3(i\text{-}C_4H_9)_2SiH$ and $CH_3(i\text{-}C_3H_7)_2SiH$ indicates that in equilibrium competitive reactions leading to conversion of π-complex to σ-complex the increase in the bulkiness of the substituents on silicon shifts the equilibrium in formation of complex *V* (Scheme 1, the other ligands are omitted).



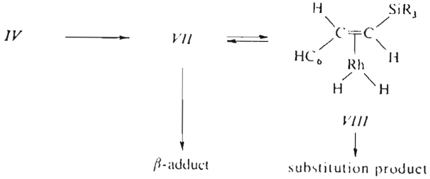
SCHEME 1

The substitution product is formed together with the β-adduct. Formation of these two products can be explained by decomposition of transition complex *V* which leads to the substitution product *via* β-elimination of hydrogen. The hydrogen coordinates to the rhodium to give dihydridorhodium(III) species which *via* formation of h^2-complex with styrene (analogous to complex *IV* except that $(CH_3)R_2Si$ ligand is in place of H) and its transformation into h^1-complex yields ethylbenzene. With increasing branching of the alkyl chain of substituents on silicon the R_3Si—Rh bond strength decreases[14,15], which may result in that trialkylsilyl group migrates as the first one (Scheme 2). Analogously to the above reaction model two isomeric



SCHEME 2

complexes are formed. Decomposition of complex *VI* leads to the α-adduct and that of complex *VII* yields both the β-adduct and the substitution product. Complex *VII* is energetically favoured transition state for formation of substitution product compared to complex *V* (only one C—H bond is cleaved). Formation of the substitution product from complex *VII* may proceed *via* another h^2-complex *VIII* (Scheme 3).



SCHEME 3

The ratio of the β-adduct to substitution product is then dependent on the relative stabilities of complexes *VII* and *VIII*. With increasing stability of complex *VIII* the yield of substitution product increases, too. This reaction model proposed for substitution of ethylene by organosilicon hydrides catalysed[13] by $[Fe(CO)_5]$ predicts also formation of isomeric substitution product* from complex *VI*. This substance has not been found among hydrosilylation products in our experiments.

The absence of the α-adduct among reaction products of the hydrosilylation carried out without benzene seems to be related to the dependence of the stability of the transition complex leading to the α-adduct *via* its decomposition on solvation by benzene. Solvation by benzene plays likely also a role in stabilization of transition states in hydrogenation of styrene, which results in that in the reaction carried out in the absence of solvent all hydrogen evolved by the addition-elimination reaction is not consumed by hydrogenation of styrene.

The reaction of 2-phenyl-1-propene with diethylmethylsilane catalysed by complex *I* yields 1-diethylmethylsilyl-2-phenylpropane (β-adduct) and two substitution products, 1-diethylmethylsilyl-2-phenyl-1-propene and 3-diethylmethylsilyl-2-phenylpropene (Eq. (*B*)).

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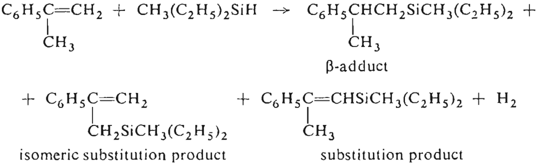
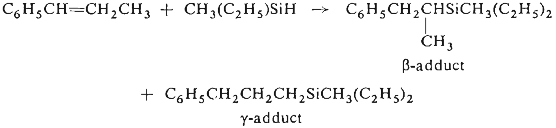
* With respect to the mechanism proposed for formation of *trans*-1-diethylmethylsilyl-2-phenylethylene, the term addition-elimination product is more appropriate then the substitution product. The latter term (Eq. (*A*)) was used frequently in literature (*cf.*[11]).



$$C_6H_5\underset{\displaystyle CH_3}{C}{=}CH_2 + CH_3(C_2H_5)_2SiH \rightarrow \underset{\beta\text{-adduct}}{C_6H_5\underset{\displaystyle CH_3}{C}HCH_2SiCH_3(C_2H_5)_2} + \underset{\text{isomeric substitution product}}{C_6H_5\underset{\displaystyle CH_2SiCH_3(C_2H_5)_2}{C}{=}CH_2} + \underset{\text{substitution product}}{C_6H_5\underset{\displaystyle CH_3}{C}{=}CHSiCH_3(C_2H_5)_2} + H_2 \qquad (B)$$

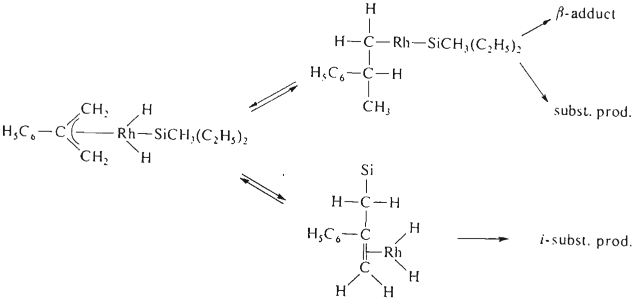
trans-1-Phenyl-1-propene reacts with diethylmethylsilane in the presence of complex *I* to form two addition products: 2-diethylmethylsilyl-1-phenylpropane and 1-diethylmethylsilyl-3-phenylpropane (Eq. (*C*)).



$$C_6H_5CH{=}CH_2CH_3 + CH_3(C_2H_5)SiH \rightarrow \underset{\beta\text{-adduct}}{C_6H_5CH_2\underset{\displaystyle CH_3}{C}HSiCH_3(C_2H_5)_2} + \underset{\gamma\text{-adduct}}{C_6H_5CH_2CH_2CH_2SiCH_3(C_2H_5)_2} \qquad (C)$$

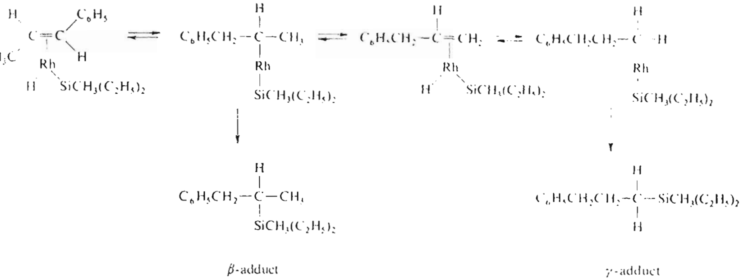
Along with the change in the structure of organosilicon products due to substitution of hydrogen of the double bond of styrene by methyl group, there proceeds also the change in the conversion of phenylalkene and the composition of organosilicon products in dependence on temperature (Table IV). These differences can be most probably related to the lower stability of h^2-alkene–rhodium complexes containing 2-phenyl-1-propene and *trans*-1-phenyl-1-propene as ligands.

Formation of the isomeric substitution product in the reaction of 2-phenyl-1-propene with diethylmethylsilane justifies the assumption about h^3-allylic type of the rhodium–2-phenyl-1-propene complex (Scheme 4).



SCHEME 4

No substitution products have been detected among products of the reaction of *trans*-1-phenyl-1-propene with diethylmethylsilane. This indicates that the γ-adduct is formed rather by isomerisation *via* h^2-allyl complex than *via* h^3-allyl species (Scheme 5).



SCHEME 5

In the presence of oxygen the reaction of styrene with trialkylsilicon hydrides catalysed by complex *I* in benzene proceeds at a faster rate with an increase in the yield of the α-adduct. This is accompanied by oxidation of the silane to disiloxane, decomposition of the catalyst to form metallic rhodium. The reaction on air is not inhibited by excess triphenylphosphine. In the presence of air the excess of styrene does not suppress α-adduct formation but leads only to increase in the yield of the substitution product in the expense of the β-adduct. Yield of the α-adduct decreases with increasing temperature both under argon (Table IV) and on air (Table V). This most likely results from the lowering of the stability of the transition complex, the decomposition of which leads to the α-adduct. The yield of the α-adduct formed from styrene and diethylmethylsilane depends more strongly on catalyst concentration and solvent than on reaction temperature (Table VI). On using catalyst concentration of $5 . 10^{-3}$ mol/l and without solvent, oxygen exerts only very small effect on products composition. The increased yield of the α-adduct and of styrene conversion due to the presence of oxygen was observed also in the reaction of styrene with diisopropylmethylsilane and diisobutylmethylsilane in benzene (Table VII). Even in the presence of oxygen triisopropylsilane does not react with styrene in benzene solution. Compared to the reaction without solvent carried out in an inert atmosphere, conversion of styrene in its reaction with triisopropylsilane increased from 55% to 100% by the effect of oxygen (*I*/styrene molar ratio = $5 . 10^{-3}$), but other reaction products than *trans*-2-triisopropylmethylsilyl-1-phenylethylene have not been detected.

The presence of oxygen in the reaction of diethylmethylsilane with 2-phenyl-1-propene and *trans*-1-phenyl-1-propene increased conversion of phenylalkenes and organosilicon products formed were exclusively corresponding β-adducts (Table VIII).

TABLE IV

The Effect of Temperature on Hydrosilylation of Phenylalkenes by Diethylmethylsilane Catalysed by Complex *I*

Phenylalkene/$CH_3(C_2H_5)_2SiH$ molar ratio = 1, *I*/the alkene molar ratio = 10^{-6}, 6 h. The catalyst added as 8·7 . 10^{-4} mol/l benzene solution.

°C	X, %	Composition of organosilicon products, %				
		α-adduct	β-adduct	A[a]	B[b]	γ-adduct
			Styrene[c]			
40	4·3	19·5	60·0	20·5	—	—
60	40·5	36·8	49·9	13·3	—	—
70	98·0	29·1	56·9	14·0	—	—
80	100·0	13·6	58·5	27·7	—	—
100	100·0	7·2	58·5	34·3	—	—
			2-Phenyl-propene[d]			
40	7·6	—	69·2	4·5	26·9	—
60	9·03	—	71·6	3·9	23·9	—
70	7·0	—	69·2	1·6	30·1	—
80	7·0	—	67·2	2·9	29·1	—
100	4·8	—	42·5	9·7	47·8	—
			trans-1-Phenyl-1-propene[d]			
40	4·0	—	79·8	—	—	20·1
60	18·2	—	90·2	—	—	9·8
70	13·3	—	74·0	—	—	25·1
80	11·5	—	74·0	—	—	26·0
100	6·7	—	51·6	—	—	48·4

[a] Substitution products (Eq. (*B*). [b] Isomeric substitution product (Eq. (*B*)). [c] All hydrogen evolved by the addition–elimination reaction leading to the substitution products reacted with styrene to give ethylbenzene. [d] Hydrogenation proceeded to less than 1 per cent.

In order to specify the catalytically active species we performed the reaction of styrene with diethylmethylsilane in the presence of oxidized benzene solution of complex *I* and in the presence of $[RhClO_2\{P(C_6H_5)_3\}_2]_2$ which was obtained[21]

TABLE V

The Effect of Temperature on the Reaction of Styrene with Diethylmethylsilane Catalysed by Complex *I* in the Presence of Air

Reaction conditions see Table IV.

°C	Composition of organosilicon products, %		
	α-adduct	β-adduct	A[a]
40	66·5	32·0	1·5
60	65·0	32·5	2·5
80	56·4	36·8	6·8
100	49·1	40·7	10·2

[a] Substitution product (Eq. (*A*)). Conversion of styrene at 40°C was 56·4 per cent. See footnote [c] in Table IV.

TABLE VI

The Effect of Oxygen on the Reaction of Styrene with Diethylmethylsilane (6 h) in Benzene

I/styrene molar ratio	Silane/ styrene molar ratio	Gaseous phase	°C	X, %	Composition of organosilicon products, %			
					α-adduct	β-adduct	A[a]	Y[b]
$2 . 10^{-4}$	1	air	70	100	46·7	43·5	9·7	1
$5 . 10^{-3,c}$	1	air	60	100	0	68·4	31·6	1·1
$2 . 10^{-4}$	1	argon	60	89·7	0	86·2	13·8	1·3
$5 . 10^{-3,c}$	1	argon	60	93·2	0	63·5	36·5	1·1
$1 . 10^{-4}$	1/5	air	70	100[d]	46·6	36·6	16·8	1·2
$1 . 10^{-4}$	1/5	argon	70	90[d]	0	51·6	48·4	1·0
$1 . 10^{-4,c}$	1	argon	70	0	0	0	0	—
$1 . 10^{-4,e}$	1	air	70	100	52·3	38·5	8·2	1

[a] Substitution product (Eq. *A*)). [b] See footnote[b] in Table II. [c] In the absence of solvent. [d] Conversion of the silicon hydride. [e] Triphenylphosphine added to the catalyst solution ($I/P(C_6H_5)_3$ molar ratio = 1 : 5).

by oxidation of $[RhCl\{P(C_6H_5)_3\}_2]_2$ (Table IX). In all experiments the organosilicon products contained greater amounts of the α-adducts compared to those obtained by the reaction catalysed by complex *I* in an inert atmosphere. Similar

TABLE VII

The Effect of Air Oxygen on the Reaction of Styrene with Trialkylsilicon Hydrides Catalysed by Complex *I*

I/styrene molar ratio = 10^{-4}, 60°C, 6 h, the catalyst added as 8·7 . 10^{-4} mol/l benzene solution.

Silicon hydride	X, %[a]	Composition of organosilicon products, %		
		α-adduct	β-adduct	A[b]
	Under argon			
$CH_3(C_2H_5)_2SiH$	40·5	36·8	49·9	13·5
$CH_3(i\text{-}C_3H_7)_2SiH$	25·7	1·5	33·4	65·1
$CH(i\text{-}C_4H_9)_2SiH$	34·3	18·1	57·7	14·2
	On air			
$CH_3(C_2H_5)_2SiH$	100	65·0	32·5	2·5
$CH_3(i\text{-}C_3H_7)_2SiH$	100	4·3	56·2	39·5
$CH_3(i\text{-}C_4H_9)_2SiH$	100	33·5	58·2	8·3

[a] Conversion of styrene. [b] Substitution product (Eq. (*A*)). All hydrogen evolved by the addition-elimination reaction reacted with styrene to produce ethylbenzene.

TABLE VIII

Hydrosilylations of 2-Phenyl-1-propene and *trans*-1-Phenyl-1-propene by Diethylmethylsilane in the Presence of Air

Styrene/$CH_3(C_2H_5)_2SiH$ molar ratio = 1, *I*/styrene molar ratio = 10^{-4}, 70°C, 6 h, the catalyst added as 8·7 . 10^{-4} mol/l benzene solution.

Phenylalkene	β-Adduct, %
Phenyl-1-propene	25·0
trans-1-Phenyl-1-propene	24·8

TABLE IX

The Effect of Catalysts on the Reaction of Styrene with Diethylmethylsilane in the Presence of Air

For reaction conditions see Table VIII, styrene/benzene ratio = 1 (by volume). Styrene conversion = 100%.

Catalyst	Composition of organosilicon products, %		
	α-adduct	β-adduct	A[a]
$[RhCl\{P(C_6H_5)_3\}_3]$	64·0	32·7	3·3
$[RhClO_2\{P(C_6H_5)_3\}_2]_2$	65·2	34·8	0
$[RhCl\{P(C_6H_5)_3\}_3]$[b]	55·1	36·2	8·7

[a] Substitution product (Eq. (*A*)). [b] $8{\cdot}7 . 10^{-4}$ mol/l benzene solution of the catalyst heated at 70°C for 6 h prior to using.

TABLE X

The Effect of Phosphorus-Containing Ligand of Rhodium Complexes on the Yields and Composition of Organosilicon Products

Phenylalkene/R_3SiH molar ratio = 1, *I*(*II*)/phenylalkene molar ratio = $5 . 10^{-3}$, 60°C, 6 h.

Catalyst	X, %	Composition of organosilicon products, %			
		β-adduct	A[a]	B[a]	γ-adduct
		$C_6H_5CH{=}CH_2 + (i\text{-}C_3H_7)_3SiH$			
I	0	—	—	—	—
II	14·9	—	—	100	—
		$C_6H_5C(CH_3){=}CH_2 + CH_3(C_2H_5)_2SiH$			
I	20·0	76·3	15·1	8·6	—
II	61·2	100·0	—	—	—
		$C_6H_5CH{=}CH_2CH_3 + CH_3(C_2H_5)_2SiH$			
I	16·2	64·6	—	—	26·1
II	52·0	95·2	—	—	4·8

[a] A = substitution product, B = isomeric substitution product (Eq. (*B*)).

data obtained for oxidized complex *I* and oxidized $[RhCl\{P(C_6H_5)_3\}_2]_2$ show that the precursor of the catalytically active species is $[RhClO_2\{P(C_6H_5)_3\}_2]_2$.

Lowering of the yield of the adduct in the reaction catalysed by catalyst solution in which the concentration of $[RhClO_2\{P(C_6H_5)_3\}_2]_2$ was decreased by heating on air can indicate that the α-adduct formation is controlled kinetically or that the species of the lower catalytic activity is formed by oxidation $[RhClO_2.\{P(C_6H_5)_3\}_2]_2$.

Comparison of catalytic effectiveness of complexes *I*, *II* and H_2PtCl_6 for hydrosilylation of styrene by trialkylsilicon hydrides shows that the most selective catalyst for the addition of diethylmethylsilane to styrene is chloroplatinic acid. At a temperature of 60°C, after 6 h styrene reacted quantitatively with $CH_3(C_2H_5)_2SiH$ (both reactants in equimolar ratio) to give 5·8% of the α-adduct and 94·2% of the β-adduct. Analogous addition of $(i\text{-}C_3H_7)_3SiH$ did not proceed even at elevated temperatures (100°C). At 60°C, higher conversions of phenylalkenes were obtained with the use of complex *II* than in the case of complex *I* (Table X). The increase of the temperature to 100°C did not result in the case of catalyst *II* in the higher yield of *trans*-1-triisopropylsilyl-2-phenylethylene compared to the reaction catalysed by complex *I* (Table II).

EXPERIMENTAL

Compounds Used

Diethylmethylsilane and diisobutylsilane were prepared by reported procedure[16]. Diisopropylsilane and triisopropylsilane were obtained from CH_3SiHCl_2 or $HSiCl_3$ and isopropyllithium[17]. Tri-tert-butylsilane was synthesized by condensation–reduction reaction of $t\text{-}C_4H_9Li$ with tetrafluorosilane[18]. The above organosilicon hydrides, the purity of which was verified by gas chromatography, were redistilled under argon prior to using. Styrene stabilized by hydroquinone (Kaučuk, Kralupy n/Vlt.) was washed with 15% sodium hydroxide solution and by water until neutral reaction on pH indicator. After drying with calcium(II) chloride it was rectified on a 20TP adiabatic column under reduced pressure under argon. Fraction boiling 45·5—45·7°C/2·67 kPa was collected. 2-Phenyl-1-propene (Kaučuk, Kralupy n/Vlt.) was purified in the same way as styrene. *trans*-1-Phenyl-1-propene (Ega-Chemie, GDR) was distilled under argon. $[RhCl.\{P(C_6H_5)_3\}_3]$ and $[RhCl\{P(C_6H_5)_3\}_2]_2$ (ref.[19]), along with $[\{RhCl(C_2H_4)_2\}_2]$ (ref.[20,21]) were prepared by reported procedures, as indicated. Chloroplatinic acid (hexahydrate, Kovohutě Vestec) was used as obtained.

Organosilicon Products

Organosilicon products of the reaction of styrene, 2-phenyl-1-propene and *trans*-1-phenyl-1-propene with diethylmethylsilane were obtained from the reaction mixture after distilling-off the starting compounds and and benzene under reduced pressure with the aid of preparative gas chromatography (Chrom 3 instrument). Isolation of the products of the reaction of the above compounds was made on a column (2·4 m × 6 mm) packed with 8·4% phenyl methyl silicone Oil on Chromaton N (0·20—0·25 mm particle size) at 160—170°C. The products of the reaction of styrene with diisopropylmethylsilane were isolated on a column (3·6 m × 6 mm) filled with

4% poly(ethylene glycol adipate) (PEGA 1500) on unglazed porous tiles (0·2—0·3 mm particle size). The products of the reaction of styrene with diisobutylmethylsilane and triisopropylsilane were obtained with the use of a column (3·6 m × 6 mm) packed with 12% silicone elastomer E 302 (ICI Ltd., England) on Chromaton N AW (0·2—0·25 mm).

Identification of organosilicon products was made by elemental analysis and by ^{1}H-NMR spectra (a HA spectrometer, 100 MHz) using 10% solutions of the compounds in deuterio chloroform. Chemical shifts are given in δ, tetramethylsilane was used as internal reference.

1-*Diethylmethylsilyl*-1-*phenylethane*. For $Si_1C_{13}H_{22}$ (206·4) calculated: 75·58% C, 10·74% H; found: 75·51% C, 10·61% H. ^{1}H-NMR spectrum: 7·29 (m) — C_6H_5, 1·5 (d), $J = 10$ Hz —$C_6H_5.CCH_3$, 2·53 (q), $J = 10$ Hz —C_6H_5CH, 0·5 (m) —$SiCH_3$, overlap with SiC_2H_5.

2-*Diethylmethylsilyl*-1-*phenylethane*. For $Si_1C_{13}H_{22}$ (206·4) calculated: 75·50% C, 10·74% H; found: 75·75% C, 10·72% H. ^{1}H-NMR spectrum: 7·32 (m) —C_6H_5, 2·51 (t), $J = 3$ Hz —$C_6H_5.CH_2$, (t) —CH_2Si, overlap, 0·92 (s) —$SiCH_3$.

trans-2-*Diethylmethylsilyl*-1-*phenylethylene*. For $Si_1C_{13}H_{20}$ (204·4) calculated: 76·39% C, 9·86% H; found: 76·21% C, 9·85% H. ^{1}H-NMR spectrum: 7·33 (m) —C_6H_5, 6·22 (d), $J =$ $= 20$ Hz —C_6H_5CH, 6·73 (d), $J = 20$ Hz —C_6H_5CHCH, 0·5 (m) —$SiCH_3$, overlap with SiC_2H_5.

1-*Diisopropylmethylsilyl*-1-*phenylethane*. For $Si_1C_{15}H_{26}$ (234·5) calculated: 76·84% C, 11·98% H found 76·79% C, 11·93% H. ^{1}H-NMR spectrum: 7·3 (m) —C_6H_5, 4·75 (q), $J = 9·5$ Hz —$C_6H_5.CH$, 1·2 (d), $J = 11$ Hz —$CHCH_3$, 1·01 (m) -i-C_3H_7, 0·08 (s) —$SiCH_3$.

2-*Diisopropylmethylsilyl*-1-*phenylethane*. For $Si_1C_{15}H_{26}$ (234·5) calculated: 76·84% C, 11·98% H; found: 76·90% C, 12·01% H. ^{1}H-NMR spectrum: 7·3 (m) —C_6H_5, 2·65 (t), $J = 3·5$ Hz —$C_6H_5CH_2$, 1·0 (deg. m) —CH_2Si + i-C_3H_7, 0·5 (s) —$SiCH_3$.

trans-2-*Diisopropylmethylsilyl*-1-*phenylethylene*. For $Si_1C_{15}H_{24}$ (232·4) calculated: 77·51% C, 11·41% H; found: 77·60% C, 10·40% H. ^{1}H-NMR spectrum: 7·37 (m) —C_6H_5, 6·41 (d), $J =$ $= 19$ Hz —C_6H_5CH, 6·81 (d), $J = 19$ Hz —$CH{=}CHSi$, 1·01 (deg. m) -i-C_3H_7, 0·4 (s) —$SiCH_3$.

1-*Diisobutylmethylsilyl*-1-*phenylethane*. For $Si_1C_{17}H_{30}$ (262·5) calculated: 77·78% C, 11·52% H; found: 77·61% C, 11·50% H. ^{1}H-NMR spectrum: 7·21 (m) —C_6H_5, 2·29 (q), $J = 7·5$ Hz —C_6H_5CH, 1·76 (h), $J = 6·5$ Hz —$CH(CH_3)_2$, 1·39 (d), $J = 7·5$ Hz —$C_6H_5CHCH_2$, 0·92 (d), $J = 7$ Hz —$SiCH_2CH(CH_3)_2$, 0·56 (d), $J = 6$ Hz —$SiCH_2$, 0·1 (s) —$SiCH_3$.

2-*Diisobutylmethylsilyl*-1-*phenylethane*. For $Si_1C_{17}H_{30}$ (262·5) calculated: 77·78% C, 11·52% H; found: 77·57% C, 11·43% H. ^{1}H-NMR spectrum: 7·18 (m) —C_6H_5, 2·61 (t), $J = 3·5$ Hz —$C_6H_5.CH_2$, 1·76 (h), $J = 6·5$ Hz —$CH(CH_3)_2$, 0·97 (d), $J = 6·5$ Hz —$CH(CH_3)_2$, 0·9 (t) — overlap $SiCH_2CH_2$, 0·61 (d), J 6·5 Hz —$SiCH_2CH$, 0·07 (s) —$SiCH_3$.

trans-2-*Diisobutylmethylsilyl*-1-*phenylethylene*. For $Si_1C_{17}H_{28}$ (260·5) calculated: 77·51% C, 10·41% H; found: 77·62% C, 10·32% H. ^{1}H-NMR spectrum: 7·28 (m) —C_6H_5, 6·84 (d), $J =$ $= 19·7$ Hz —$CH{=}CHSi$, 6·39 (d), $J = 19·5$ Hz —C_6H_5CH, 1·78 (h), $J = 6·3$ Hz —$SiCH_2.CH(CH_3)_2$, 0·91 (d), $J = 6·8$ Hz —$CH(CH_3)_2$, 0·62 (d), $J = 6·9$ Hz —$SiCH_2$, 0·14 (s) —$SiCH_3$.

trans-2-*Triisopropylsilyl*-1-*phenylethylene*. For $Si_1C_{17}H_{28}$ (260·5) calculated: 77·51% C, 10·41% H; found: 77·79% C, 10·78% H. ^{1}H-NMR spectrum: 7·32 (m) —C_6H_5, 6·98 (d), $J =$ $= 19·2$ Hz —$CH{=}CHSi$, 6·35 (d), $J = 19·3$ Hz —C_6H_5CH, 1·1 (deg. m) -i-C_3H_7.

1-*Diethylmethylsilyl*-2-*phenylpropane*. For $Si_1C_{14}H_{24}$ (220·4) calculated: 76·28% C, 10·97% H; found: 75·98% C, 10·81% H. ^{1}H-NMR spectrum: 7·21 (m) —C_6H_5, 2·88 (q), $J = 7$ Hz —$C_6H_5.CH$, 1·31 (d), $J = 6·8$ Hz —$C_6H_5CH_3$, 0·92 (m) —$SiCH_2CH_3$, 0·82 (s) —$C_6H_5CHCH_2Si$, 0·43 (m) —SiCH$_2$CH$_3$, 0·18 (s) —SiCH$_3$. ^{13}C-NMR spectrum: $\delta =$ 128·26; 126·57; 125·79 — (*o*-, *m*-, *p*-CH), $\delta =$ 150·09 (C *ipso*), $\delta =$ 36·26 (C$_6$H$_5$CH), $\delta =$ 26·51 (C$_6$H$_5$CHCH$_3$), $\delta =$ = 23·39 (CHCH$_2$Si), $\delta =$ −5·59 (SiCH$_3$), $\delta =$ 5·59 (Si(CH$_2$CH$_3$), $\delta =$ 7·28 —(SiCH$_2$CH$_3$).

1-*Diethylmethylsilyl*-2-*phenyl*-1-*propene*. For Si$_1$C$_{14}$H$_{22}$ (218·4) calculated: 76·11% C, 10·15% H; found: 75·77% C, 10·04% H. ^{1}H-NMR spectrum: 7·31 (m) —C$_6$H$_5$, 5·82 (s) —CHSi, 2·21 (s) —C$_6$H$_5$CCH$_3$, 0·98 (d), $J =$ 13·9 Hz —SiCH$_2$CH$_3$, 0·74 (m) —SiCH$_2$, 0·15 (s) —SiCH$_3$.

3-*Diethylmethylsilyl*-2-*phenyl*-1-*propene*. For Si$_1$C$_{14}$H$_{22}$ (218·4) calculated: 76·11% C, 10·15% H, found: 75·82% C, 10·11% H. ^{1}H-NMR spectrum: 7·26 (m) —C$_6$H$_5$, 4·98 (d), $J =$ 22·5 Hz —CH$_2$=CC$_6$H$_5$, 2·02 (s) —CCH$_1$Si, 0·85 (m) —SiCH$_2$CH$_3$, 0·44 (m) —SiCH$_2$CH$_3$, −0·18 (s), —SiCH$_3$.

2-*Diethylmethylsilyl*-1-*phenylpropene*. For Si$_1$C$_{14}$H$_{24}$ (220·4) calculated: 76·28% C, 10·97% H; found: 75·95% C, 10·91% H. ^{1}H-NMR spectrum: 7·1 (m) —C$_6$H$_5$, 1·87 (deg. m.) —C$_6$H$_5$.CH$_2$CH, 0·83 (deg. m) —CCH$_3$, 0·51 (m) —SiCH$_2$, −0·1 (s) —SiCH$_3$.

1-*Diethylmethylsilyl*-1-*phenylpropene*. For Si$_1$C$_{14}$H$_{24}$ (220·4) calculated: 76·28% C, 10·97% H; found: 75·61% C, 10·8% H. ^{1}H-NMR spectrum: 7·18 (m) —C$_6$H$_5$, 2·63 (t), $J =$ 3·5 Hz —C$_6$H$_5$.CH$_2$, 1·64 (m) —C$_6$H$_5$CH$_2$CH$_2$, 0·91 (deg. m) —CH$_2$CH$_3$, 0·52 (m) —SiCH$_2$, —0·09 (s) —SiCH$_3$.

All experiments were carried out in sealed ampoules with degassed reactants and solvent. The ampoules were heated in a thermostated bath and shaken with a mechanical vibrator. After completion of the reaction, the ampoules were cooled by dry ice and analysed by gas chromatography (a thermal ionisation detector, 9% phenyl methyl silicone oil DC 550 (Becker, GFR) on Chromaton N (0·2 mm). The column temperature was increased at a rate of 3°C/min from 80 to 170°C. Isomerisation of organosilicon compounds was followed under the same conditions as hydrosilylation. It was found that within experimental errors the isomerisation of organosilicon products does not take place.

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