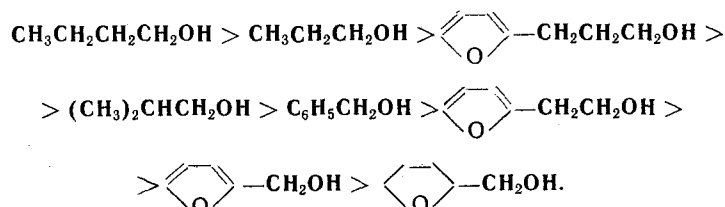


ORGANOSILICON COMPOUNDS OF THE FURAN SERIES
VII*. DEHYDROCONDENSATION OF ALCOHOLS WITH
TRIORGANYLSILANES IN THE PRESENCE OF H_2PtCl_6

E. A. Lukevits and M. G. Voronkov

Khimiya Geterotsiklicheskikh Soedinenii, Vol. 1, No. 2, pp. 171-178, 1965

The kinetics of dehydrocondensations between triethylsilane and various alcohols are investigated. Alcohol reactivity decreases on passing from primary to secondary, and from secondary to tertiary alcohols. The reaction rate for primary alcohols decreases in the order



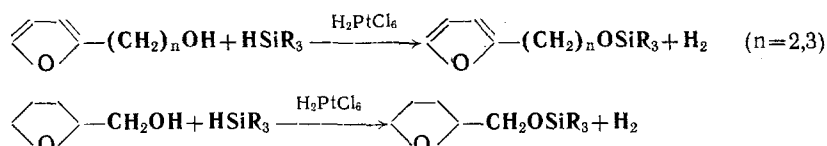
Dehydrocondensation is slower in dioxane than in toluene, and the rates in pyridine and dimethylformamide are even lower.

It is suggested that reaction proceeds via formation of cyclic activated complexes at the catalyst surface.

A series of new 2-(2-furyl)ethoxy-, 3-(2-furyl)propoxy-, and tetrahydrofurfuryloxysilanes are obtained.

A convenient method for obtaining various alkoxy silanes [2-8] is dehydrocondensation of hydroxysilanes with alcohols in the presence of catalytic quantities of $H_2PtCl_6 \cdot 6H_2O$, and the present authors previously used it to synthesize furfuryloxysilanes [7].

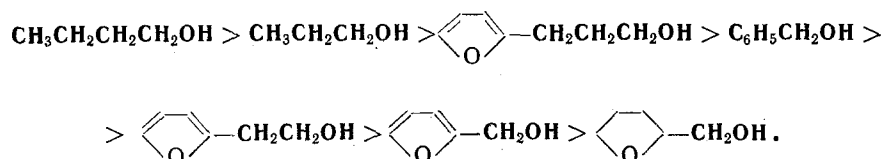
The present paper describes the dehydrocondensation of triorganylsilanes with β -(2-furyl)ethanol, 3-(2-furyl)propanol, and tetrahydrofurfuryl alcohol. These reactions give high yields (90-93%) of the corresponding triorganylsiloxy derivatives



The rates of dehydrocondensation of hydroxysilanes with alcohols depend on the structures of the two reactants, the solvent nature, and the amount of catalyst**.

By changing one of these factors while keeping the others constant, it is possible to determine separately the effect of each on the progress of the dehydrocondensation reaction.

To accomplish this, and also to compare the reactivities of alcohols of the furan and tetrahydrofuran series with those of aliphatic alcohols, araliphatic alcohols, carbocyclic alcohols, and phenols, a study was made of the kinetics of dehydrocondensation of triethylsilane with a series of alcohols under identical conditions (standard concentrations of reagents, catalyst, and solvent, temperature constant). Measurement of the rate of hydrogen evolution made it possible to compare rates for the actual dehydrocondensation reaction of the different alcohols. In this way it was established that the reactivities of primary alcohols towards triethylsilane in toluene at 25° decrease in the following order (Fig. 1, Table 1):



* For Part VI see [1].

** Side reactions are caused by traces of moisture and the presence of other functional groups in the alcohol molecule.

Thus replacement of the γ hydrogen atom in the n-propanol molecule by a methyl group with a +I effect accelerates dehydrocondensation, while introduction of the α -furyl group, with a -I effect, slows it down. Separation of the α -furyl group from the hydroxyl, or replacement of it by a phenyl group, which has a smaller -I effect*, increases the rate of dehydrocondensation. Hence the higher the electron density at the hydroxyl group oxygen atom, in the alcohol molecule, the faster the reaction. Comparison of rates of dehydrocondensation of triethylsilane with phenol and cyclohexanol confirms this. Phenol, where the electron density at the oxygen is decreased through conjugation with the benzene nucleus, reacts much less readily with hydroxyls than does cyclohexanol. At the same time acids are more

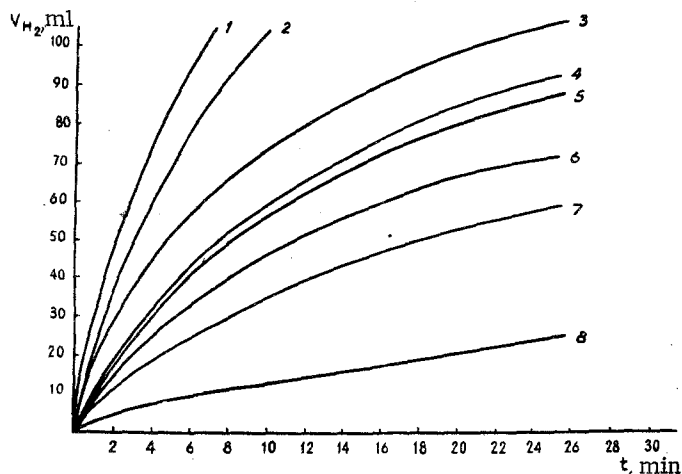
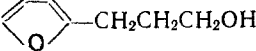
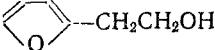
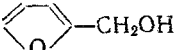
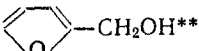
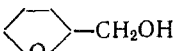


Fig. 1. Rate of hydrogen evolution in the dehydrocondensation of triethylsilane with alcohols (25°) as a function of their structure (molar ratio of catalyst: $(C_2H_5)_3SiH:ROH$ is $1.25 \cdot 10^{-6}$; $1 \cdot 10^{-2}$; $1 \cdot 10^{-2}$, total volume of solution in toluene 5 ml): 1 - n-butyl, 2 - n-propyl, 3 - 3-furylpropyl, 4 - isobutyl, 5 - benzyl, 6 - 2-furylethyl, 7 - furfuryl, 8 - tetrahydrofurfuryl.

TABLE 1

Rate constants for the dehydrocondensation reaction between alcohols and triethylsilane in the presence of $H_2PtCl_6 \cdot 6H_2O$ in toluene at 25°. *

Alcohol	$k_2^{25} \cdot 10^{-4}$ l/mole·sec	Rate of alcoholysis of decaborane in benzene, [10], $k_2 \cdot 10^{-7}$ l/mole·sec	Solubility HCl [11], mole/mole
$CH_3CH_2CH_2CH_2OH$	8.93 ± 0.38	6.70	0.964
$CH_3CH_2CH_2OH$	6.85 ± 0.35	5.35	0.956
 $CH_2CH_2CH_2OH$	4.08 ± 0.48		
$(CH_3)_2CHCH_2OH$	2.77 ± 0.12	4.79	0.972
$C_6H_5CH_2OH$	2.58 ± 0.09	2.86	0.812
 CH_2CH_2OH	1.99 ± 0.20		
 CH_2OH	1.52 ± 0.15		
 CH_2OH^{**}	0.61 ± 0.06		
 CH_2OH	0.39 ± 0.02		

* Molar ratio catalyst:triethylsilane:alcohol = $1.25 \cdot 10^{-6}$; $1 \cdot 10^{-2}$; $1 \cdot 10^{-2}$.

** In dioxane; molar ratio alcohol:triethylsilane 2:1.

reacts much less readily with hydroxyls than does cyclohexanol. At the same time acids are more

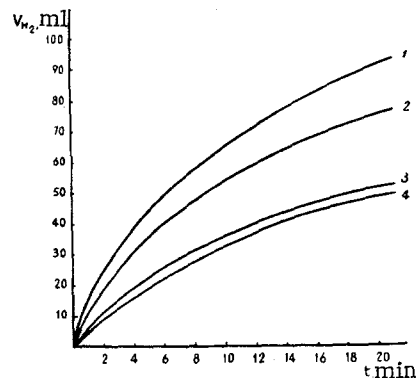


Fig. 2. Rate of hydrogen evolution when furfuryl alcohol reacts with triethylsilane, as a function of their molar ratios (in toluene at 25°): 1 - 2:1; 2 - 1.5:1; 3 - 1:1; 4 - 2:1 (in dioxane)

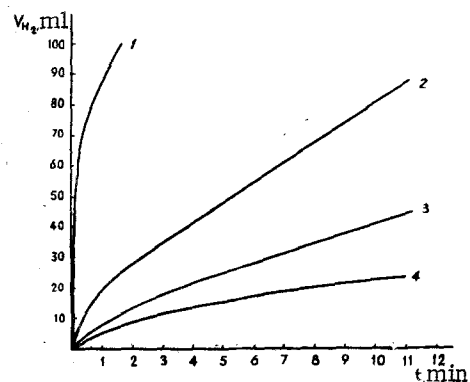


Fig. 3. Rate of hydrogen evolution when triethylsilane reacts with alcohols (65°), as a function of the alcohol structure (molar ratio of catalyst: $(C_2H_5)_3SiH:ROH = 2.5 \cdot 10^{-6}$; $0.5 \cdot 10^{-2}$; $1.0 \cdot 10^{-2}$; total volume of solution in dioxane 3 ml): 1 - water (30°, molar ratio of reactants 1:1), 2 - benzyl alcohol, 3 - furfuryl alcohol, 4 - tetrahydrofurfuryl alcohol.

* Here the electronegativity of the α -furyl group was found from IR spectra data for furylsilanes. A separate paper will be devoted to this subject.

TABLE 2

Rate constants for the dehydrocondensation reaction between triethylsilane and the isomeric butanols in the presence of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ at 40° and 60°.*

Alcohol	Solvent	Reaction temperature °C	$k_2 \cdot 10^{-4}$ l/mole·sec	Rate constants of alcoholysis of decaborane in benzene [10], $k_2 \cdot 10^{-4}$ l/mole·sec	Solubility HCl, mole/mole [11]
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	Toluene	40	25.72 ± 1.05	6.70	0.964
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	Dioxane	40	9.26 ± 0.88		
$(\text{CH}_3)_2\text{CHCH}_2\text{OH}$	Toluene	40	9.78 ± 0.60	4.79	0.972
$(\text{CH}_3)_2\text{CHCH}_2\text{OH}$	Dioxane	40	2.31 ± 0.34		
$\text{CH}_3\text{CH}_2(\text{CH}_3)\text{CHOH}$	Toluene	60	0.44 ± 0.04	3.80	1.048
$(\text{CH}_3)_3\text{COH}$	Toluene	60	0.10 ± 0.01	0.09	1.115

* Molar ratio catalyst:triethylsilane:alcohol = $2.5 \cdot 10^{-6}:0.5 \cdot 10^{-2}:1.0 \cdot 10^{-2}$.

TABLE 3

Rate constants for the dehydrocondensation reaction between triethylsilane and furylcarbinols in the presence of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ at 75°.*

Alcohol**	$k_2^{75} \cdot 10^{-4}$ l/mole·sec
RCH_2OH	13.50 ± 0.20
RCHOHCH_3	1.05 ± 0.09
$\text{RCHOHCH}_2\text{CH}_3$	0.61 ± 0.03
$\text{RCHOHCH}_2\text{CH}_2\text{CH}_3$	0.49 ± 0.03

* Molar ratio catalyst:triethylsilane:alcohol = $5 \cdot 10^{-6}:1.0 \cdot 10^{-2}:1.0 \cdot 10^{-2}$.

** R = 2-furyl.

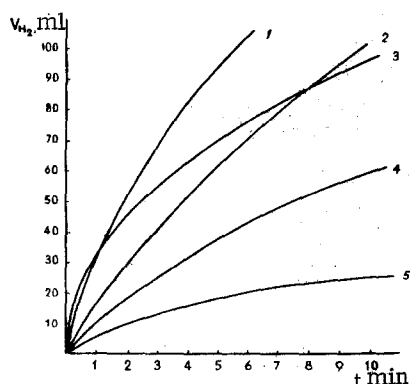


Fig. 4. Rate of hydrogen evolution when triethylsilane reacts with alcohols (75°), as a function of their structures (molar ratio catalyst: $(\text{C}_2\text{H}_5)_3\text{SiH}:\text{ROH} = 2.5 \cdot 10^{-6}:0.5 \cdot 10^{-2}:1.0 \cdot 10^{-2}$, total solution volume 3 ml): 1 - benzyl (in toluene), 2 - furfuryl (in toluene), 3 - benzyl (in dioxane), 4 - furfuryl (in dioxane), 5 - tetrahydrofurfuryl (in dioxane).

TABLE 4

Rate constants for the dehydrocondensation reaction between triethylsilane and cyclohexanol, phenol, acetic and pyromucic acids in the presence of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ at 75°.*

Hydroxyl compound	Solvent	$k_2^{75} \cdot 10^{-4}$ l/mole·sec
$\text{C}_6\text{H}_{11}\text{OH}$	Toluene	2.22 ± 0.14
$\text{C}_6\text{H}_5\text{OH}$	Toluene	0.095 ± 0.010
CH_3COOH	Toluene	1.11 ± 0.01
RCOOH^{**}	Dioxane	0.70 ± 0.03

* Molar ratio catalyst:triethylsilane:ROH = $3.75 \cdot 10^{-6}:0.5 \cdot 10^{-2}:1.0 \cdot 10^{-2}$.

** R = 2-furyl. Molar ratio catalyst:triethylsilane:acid = $3.75 \cdot 10^{-6}:0.5 \cdot 10^{-2}:0.5 \cdot 10^{-2}$.

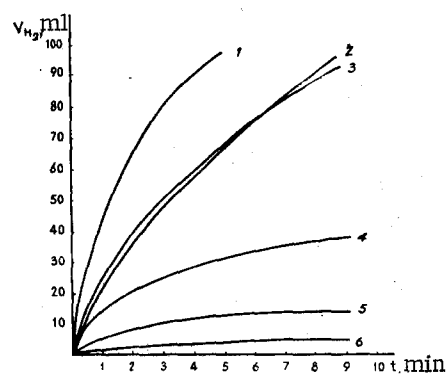
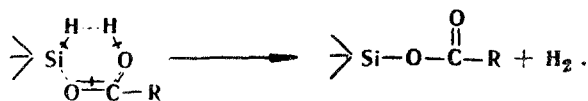


Fig. 5. Rate of hydrogen evolution when triethylsilane reacts with the isomeric butanols (molar ratio catalyst: $(\text{C}_2\text{H}_5)_3\text{SiH}:\text{ROH} = 2.5 \cdot 10^{-6}:0.5 \cdot 10^{-2}:1.0 \cdot 10^{-2}$; 3 ml solution) at 40°: 1 - n-butanol (in toluene), 2 - n-butanol (in dioxane), 3 - isobutanol (in toluene), 4 - isobutanol (in dioxane), 5 - sec. butanol (in toluene at 60°), 6 - tert. butanol (in toluene at 60°).

reactive than phenol, since with them there can be nucleophilic attack by the carbonyl oxygen (Fig. 7, Table 4):



However, the different reactivities displayed by alcohols in dehydrocondensation with triethylsilane cannot be explained just by electronic effects. Contrary to what would be expected from the increased basicity of the alcohols, the rate of dehydrocondensation does not increase on passing from primary to secondary, and from secondary to tertiary alcohols, or with increased branching of the carbon chain, but decreases. Thus in reaction with triethylsilane at 40° in toluene or dioxane the reactivities of the isomeric butanols decrease in the following order (Fig. 5, Table 2):

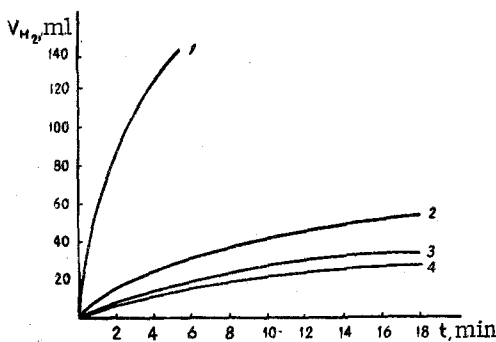
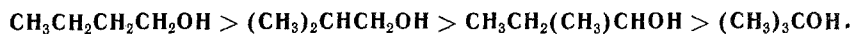


Fig. 6. Rate of hydrogen evolution when triethylsilane reacts with furylalkylcarbinols (molar ratio catalyst: $(\text{C}_2\text{H}_5)_3\text{SiH}:\text{ROH} = 5 \cdot 10^{-6}:1 \cdot 10^{-2}$; $:1 \cdot 10^{-2}$, total solvent volume 3 ml) at 75°: 1 - furfuryl, 2 - furylmethylcarbinol, 3 - furylethylcarbinol, 4 - furylpropylcarbinol.

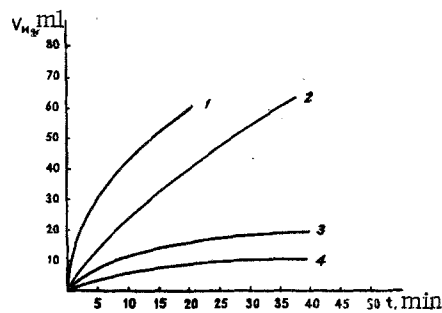
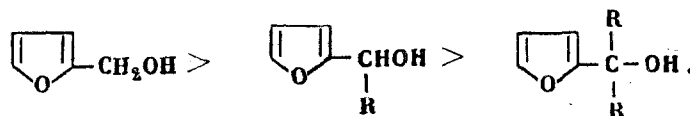
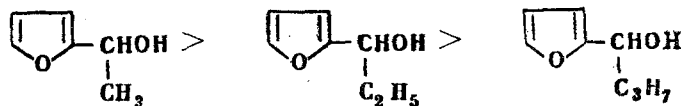


Fig. 7. Rate of hydrogen evolution when triethylsilane reacts with hydroxylic compounds (molar ratio catalyst: $(\text{C}_2\text{H}_5)_3\text{SiH}:\text{ROH} = 3.75 \cdot 10^{-6}:$ $:0.5 \cdot 10^{-2}; 1 \cdot 10^{-2}$) in toluene at 75°: 1 - cyclohexanol, 2 - acetic acid, 3 - pyromucic acid (in dioxane, molar ratio of reactants 1:1), 4 - phenol.

The same order is observed in the furan series



Reaction velocity also decreases with increased length of the side chain in secondary alcohols (Fig. 6, Table 3):



Consequently, alcohol reactivities are functions not only of electronic factors, but to a considerable extent of steric ones, too. In this connection, it may be mentioned that water reacts faster with hydrosilanes than alcohols (Fig. 3).*

The observed regularity in dehydrocondensation between alcohols and triethylsilanes falls into line with data on the reactivity of alcohols towards decaborane [10].

Tables 1 and 2 give rate constants (calculated using a second-order equation) for dehydrocondensation of alcohols with triethylsilane or decaborane [10], as well as

* Reaction of trialkylsilanes with water in the presence of H_2PtCl_6 is a simple and convenient method of synthesizing trialkylsilanols [9].

TABLE 5.
2- and 3-(2-furyl)alkoxy- and tetrahydrofuryloxytrialkylsilanes

Compound ^a	bp °C (pressure, mm)	n_D^{20}	d_4^{20}	MR _D		Empirical formula	Si, %		Yield %
				Found	Calculated		Found	Calculated	
$\text{RCH}_2\text{CH}_2\text{OSi}(\text{C}_2\text{H}_5)_3$	96(3)	1.4565	0.9363	65.79	66.42	$\text{C}_{12}\text{H}_{22}\text{O}_3\text{Si}$	12.11; 12.24	12.41	92.5
$\text{R}(\text{CH}_2)_3\text{OSi}(\text{C}_2\text{H}_5)_3$ ($n\text{-C}_3\text{H}_7$) ₂	127—128(3.5)	1.4580	0.9163	79.94	80.55	$\text{C}_{15}\text{H}_{28}\text{O}_3\text{Si}$	10.21; 10.16	10.46	89.4
$\text{R}'\text{CH}_2\text{OSi}(\text{C}_2\text{H}_5)_3$	91(4.5)	1.4460	0.9212	62.63	62.73	$\text{C}_{11}\text{H}_{24}\text{O}_2\text{Si}$	12.91; 12.88	12.98	90.4
$\text{R}'\text{CH}_2\text{OSi}(\text{C}_2\text{H}_5)_3$ ($n\text{-C}_3\text{H}_7$) ₂	89.5—90(1)	1.4477	0.9073	72.07	72.23	$\text{C}_{13}\text{H}_{26}\text{O}_2\text{Si}$	11.22; 11.31	11.49	93.1
$\text{R}'\text{CH}_2\text{OSi}(\text{C}_2\text{H}_5)_3$ ($n\text{-C}_4\text{H}_9$) ₂	107—109(1.5)	1.4500	0.8993	81.43	81.33	$\text{C}_{15}\text{H}_{32}\text{O}_2\text{Si}$	10.08; 10.11	10.31	91.2

base constants for the alcohols (as determined by the solubility of HCl) [11]. These results indicate that in each case both electronic and steric factors must be taken into account, to explain the change in character of the reactivities of the alcohols. At the same time dehydrocondensation of alcohols with hydrosilanes in the presence of H_2PtCl_6 is more complex, since the latter is a microheterogeneous catalyst. Moreover, the reaction rate is also dependent on the amount of catalyst, colloidal platinum, and its capacity for surface adsorption of reagents.

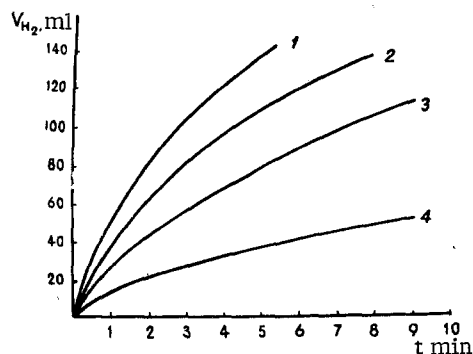


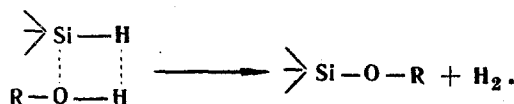
Fig. 8. Change in rate of hydrogen evolution as a function of quantity of catalyst when triethylsilane reacts with furfuryl alcohol (molar ratio $(C_2H_5)_3SiH:ROH = 1 \cdot 10^{-2}:1 \cdot 10^{-2}$) at 75°: 1 - $5 \cdot 10^{-6}$, 2 - $3.75 \cdot 10^{-6}$, 3 - $2.5 \cdot 10^{-6}$, 4 - $1.25 \cdot 10^{-6}$ mole.

Dehydrocondensation of furfuryl alcohol with triethylsilane takes place faster in toluene than in dioxane*. This reaction is considerably slowed down by pyridine and dimethylformamide. The negative effect of such solvents can be related to their possible hydrogen bonding with alcohol molecules, or forming actual complexes due to nucleophilic reaction with triethylsilane, these hindering formation of the activated reaction complex.

Further, it is by no means excluded that different solvents correspond to different catalytic systems, or that the platinum catalysts formed possess active surfaces of different sizes. In some cases the catalyst particles are observed to increase in size during reaction, and to precipitate on to the walls of the vessel when reaction is finished. Platinum black was a less effective catalyst than H_2PtCl_6 , which is reduced by the triethylsilane.

It is impossible to ignore, too, that in the presence of strongly polar solvents catalyst poisoning can occur, due to irreversible adsorption of solvent at the surface.

The observed relationships in the reaction of triethylsilane with alcohols in the presence of H_2PtCl_6 (kinetic data; increase in reaction velocity when the electron density at the oxygen atom of primary alcohols is raised, and a decrease in velocity with branching of the carbon chain in the case of secondary and tertiary alcohols; reaction rate dependent on amount of catalyst, and finally, increased dehydrocondensation velocity in non-polar or weakly polar solvents)** suggest the following hypothesis. Dehydrocondensation involves a nucleophilic attack on the silicon atom, and an electrophilic attack on the hydrogen atom in the hydrosilane, by the alcohol molecule in an activated cyclic complex formed on the surface of the catalyst:



EXPERIMENTAL

The kinetic experiments were carried out in a two-limbed vessel. In one limb were placed weighed amounts of triethylsilane and catalyst, and in the other the alcohol. The vessel was connected through a reflux condenser to a gas buret, and placed in a thermostat, where it was kept at the desired temperature (constant to within $\pm 0.1^\circ$). The reaction was carried out with continuous mechanical shaking. The amount of hydrogen evolved was read every 30 sec. Figs. 1-8 show the results obtained, these being mean values from three parallel experiments.

When hydrogen was no longer evolved from the reaction mixture, the unreacted initial reactants were distilled off, and the residue vacuum-distilled. Table 5 gives physical constants, yields, and analytical data for the new compounds obtained.

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* It has been found that dehydrocondensation is accelerated when carried out in isooctane [3].

** See [12] for the effect of solvent on the mechanism of nucleophilic substitution at a silicon atom.

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23 October 1964

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