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ORGANOSILICON COMPOUNDS OF THE FURAN SERIES VIII. REACTION OF TRIETHYLSILANE WITH UNSATURATED ALCOHOLS*

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When triethylsilane is reacted with unsaturated primary alcohols such as allyl, cinnamic, and furylallyl alcohols, in the presence of H_2PtCl_6, the main reaction is one of dehydrocondensation. With secondary unsaturated alcohols such as methylallylcarbinol and furylallylcarbinol, dehydrocondensation and hydrosilylation take place simultaneously. A number of new furylalkoxy- and furyl-alkenoxysilanes are synthesized and described.

In the presence of H_2PtCl_6 hydrosilanes readily undergo dehydrocondensation with organic compounds containing a hydroxyl group (alcohols, phenols, carboxylic acids) and with water [1-13] according to the equation

$$\geq Si-H + H-O-R \rightarrow \geq Si-O-R + H_2 .$$

Hydrosilylation also occurs in the presence of the same catalyst. This is an addition of hydrosilanes to unsaturated compounds [14]:

$$\geq Si-H + -\overset{|}{C}=\overset{|}{C}- \rightarrow \geq Si-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-H .$$

When hydrosilanes react with unsaturated hydroxylic compounds, dehydrocondensation and hydrosilylation can occur side by side. Hence the direction of the process must be determined by structural characteristics of the reactants.

Up to the present the reaction of triethylsilane with allyl alcohol in the presence of H_2PtCl_6 has not been investigated. In the presence of Pt/C, triethylsilane undergoes only dehydrocondensation with allyl alcohol, while hydrosilylation products are also formed from the latter and tributyl- and triphenylsilane.

The reaction products were not found to contain [15, 16] compounds with two silicon atoms per molecule, which could have been formed by simultaneous or consecutive hydrosilylation and dehydrocondensation

$$\geq Si-H + HO-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}=\overset{|}{\underset{|}{C}} + H-Si\leq \rightarrow \geq Si-O-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{H}{C}}-\overset{|}{\underset{|}{C}}-Si\leq + H_2 .$$

A patent [17] states that in the presence of $Pt/\gamma\text{-}Al_2O_3$, pentamethyldisoloxane undergoes dehydrocondensation with allyl alcohol. With tetramethyldisiloxane, hexamethylethyltrisiloxane, and heptamethyltrisiloxane hydrosilylation occurs, though judging by the low hydroxyl contents found analytically, traces of dehydrocondensation products may be present.

The present investigation was concerned with how the reaction of triethylsilane with unsaturated alcohols is affected by the structure of the latter. Allyl alcohol, the simplest, reacts with triethylsilane in the presence of $H_2PtCl_6 \cdot 6H_2O$ with evolution of hydrogen (~90% theoretical). The reaction, which is exothermic, starts at room temperature. Two compounds, containing one (I) silicon atom per molecule, and two (II), were isolated from the reaction products. Compound I was found not to contain a hydroxyl group, so that it was formed by dehydrocondensation:

$$CH_2=CHCH_2OH + HSi(C_2H_5)_3 \rightarrow \underset{(I)}{CH_2=CHCH_2OSi(C_2H_5)_3} + H_2 .$$

Its physical constants are the same as those of triethylalloxysilane, synthesized from allyl alcohol and triethylchlorosilane in the presence of pyridine.

Compound II can be formed by addition of a second molecule of triethylsilane to triethylalloxysilane, or by hydrosilylation of allyl alcohol with subsequent dehydrocondensation of the resultant 3-triethylsilylpropan-1-ol. Separate experiments showed that under the conditions used to react triethylsilane with allyl alcohol (20-60°; 1 hr), the former does not add to triethylalloxysilane. Some reaction is observed only when the reaction mixture is boiled (100-110°) for 24 hr. On the other hand 3-(triethylsilyl)propan-1-ol reacts as energetically with triethylsilane as does allyl alcohol. So it must be assumed that II is formed from the product of hydrosilylation of allyl alcohol according to the equation:

$$(C_2H_5)_3SiH + CH_2=CHCH_2OH \rightarrow (C_2H_5)_3SiCH_2CH_2CH_2OH$$

$$(C_2H_5)_3SiCH_2CH_2CH_2OH + HSi(C_2H_5)_3 \rightarrow (C_2H_5)_3Si(CH_2)_3OSi(C_2H_5)_3 + H_2 .$$

Some decrease in the amount of hydrogen evolved on reaction of triethylsilane with allyl alcohol may also be due to partial hydrogenation of the double bond [18]. However, it was not possible to isolate any reduction products.

Thus when triethylsilane is reacted with allyl alcohol in the presence of $H_2PtCl_6 \cdot 6H_2O$, the main reaction is dehydrocondensation (~75%), with an unimportant degree of hydrosilylation (~11%) followed by dehydrocondensation of the resultant organosilicon alcohol with a second molecule of triethylsilane.

It may be assumed that this proportion will vary depending on the structures of the hydrosilane and unsaturated alcohol, and possibly with the reaction conditions, too.

The mode of reaction is unaffected by replacing a hydrogen in the allyl alcohol molecule by a phenyl or furyl group. Reaction of cinnamic alcohol and 3-(2-furyl)allyl alcohol with triethylsilane in the presence of $H_2PtCl_6 \cdot 6H_2O$ leads to dehydrocondensation:

$$RCH{=}CHCH_2OH + HSi(C_2H_5)_3 \rightarrow RCH{=}CHCH_2OSi(C_2H_5)_3 + H_2,$$

where R is phenyl or 2-furyl.

These reactions also take place in the presence of sodium metal, though much more slowly.

The reaction products were identified by comparing their constants with those of triethyl-3-(2-furyl)alloxysilane and triethyl-3-(2-furyl)propoxysilane (and their phenyl analogs), prepared according to the equations:

$$RCH{=}CHCH_2OH + ClSi(C_2H_5)_3 \xrightarrow{C_5H_5N} RCH{=}CHCH_2OSi(C_2H_5)_3 + C_5H_5N \cdot HCl$$

$$RCH_2CH_2CH_2OH + HSi(C_2H_5)_3 \xrightarrow{H_2PtCl_6} RCH_2CH_2CH_2OSi(C_2H_5)_3 + H_2,$$

where R = 2-furyl, phenyl.

It is of interest to note that introducing the triethylsilyl group into the allyl alcohol molecule (unlike the phenyl or furyl group) cuts the velocity of dehydrocondensation to such an extent that the hydrosilylation product of propargyl alcohol, 3-triethylsilylprop-2-ene-1-ol, can be obtained in good yield:

$$(C_2H_5)_3SiH + CH{\equiv}CCH_2OH \rightarrow \underset{80\%}{(C_2H_5)_3SiCH{=}CHCH_2OH}.$$

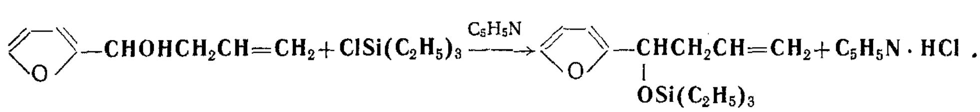
Only a small amount of the product of further dehydrocondensation is formed:

$$(C_2H_5)_3SiCH{=}CHCH_2OH + HSi(C_2H_5)_3 \rightarrow \underset{13\%}{(C_2H_5)_3SiCH{=}CHCH_2OSi(C_2H_5)_3} + H_2.$$

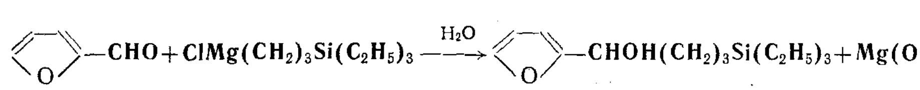
It should also be mentioned that on changing from saturated alcohols to those with a double or triple bond, the rate of dehydrocondensation is diminished, due to the –I effect of alkenyl and alkynyl groups. For example allyl alcohol reacts more slowly with triethylsilane than n-propanol. Actually in the case of propargyl alcohol, dehydrocondensation is completely replaced by hydrosilylation [19, 20].

The reactivity of alcohols in the dehydrocondensation reaction decreases in the order primary, secondary, tertiary [1]. Hence only hydrosilylation occurs [8, 14, 21-26] when unsaturated tertiary alcohols react with hydrosilanes in the presence of $H_2PtCl_6 \cdot 6H_2O$. Both dehydrocondensation and hydrosilylation occur with secondary acetylenic alcohols [8]. So far the reaction of secondary alcohol containing a double bond with hydrosilanes in the presence of $H_2PtCl_6 \cdot 6H_2O$ has not been investigated.

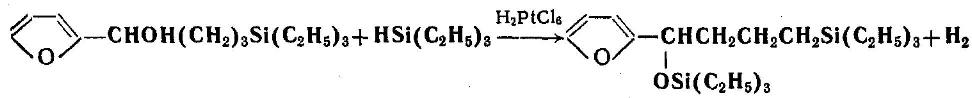
It has now been found that 4-(2-furyl)but-1-ene-4-ol undergoes reaction with triethylsilane accompanied by hydrogen evolution, only when the reaction mixture is heated to boiling. Two reaction products were obtained. To establish their structures a "counter" synthesis of all expected hydrosilylation and dehydrocondensation products was carried out. Triethyl-4-(2-furyl)but-1-ene-4-oxysilane was obtained by reacting 2-furylallylcarbinol with triethylchlorosilane in the presence of pyridine:



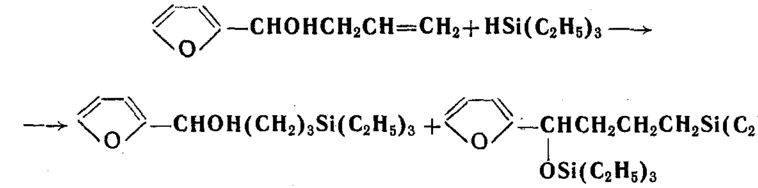
A Grignard reaction between furfural and 3-(triethylsilyl)propyl magnesium chloride gives 1-(2-furyl)-4-(triethylsilyl) butan-1-ol:



and dehydrocondensation of the latter with triethylsilane in the presence of H_2PtCl_6 converts it to triethyl-4-triethylsilyl-1-(2-furyl)butoxysilane:



Comparison of the products of reaction of 4-(2-furyl)but-1-ene-4-ol with triethylsilane with the above compounds showed that the compounds isolated were 1-(2-furyl)-4-(triethylsilyl)butan-1-ol (yield 11%), and triethyl-4-triethylsilyl-1-(2-furyl)butoxysilane (yield 24.4%):



A similar reaction of triethylsilane with pent-1-ene-4-ol gave triethylpent-1-ene-4-oxysilane and triethylsilylpentoxysilane in 28% and 36.4% yield, respectively.

Thus both dehydrocondensation and hydrosilylation take place simultaneously when triethylsilane reacts with secondary ethylenic alcohols in the presence of $H_2PtCl_6 \cdot 6H_2O$.

EXPERIMENTAL

Starting reactants. 3-chloropropyltriethylsilane is prepared in 77.3% yield from 3-chloropropylethyldichlorosilane and C_2H_5MgBr. 3-Triethylsilylpropan-1-ol is synthesized from C_2H_5MgBr and 3-acetoxypropylethyldichlorosilane, yield 70.6%. The latter compound is prepared by hydrosilylating allyl acetate with ethyldichlorosilane in the presence of $H_2PtCl_6 \cdot 6H_2O$ (yield 81.6%).

Reaction between triethylsilane and alcohols. The reaction takes place in a 3-necked flask fitted with a reflux condenser, thermometer, and dropping funnel. The triethylsilane and catalyst (0.1 M $H_2PtCl_6 \cdot 6H_2O$ in isopropanol) are put into the flask, and the alcohol is added dropwise*. Then the reaction mixture is heated. When reaction is complete the unreacted starting materials are distilled off, and the residue vacuum-distilled. The quantities of reactants and catalyst, the reaction conditions, and the product yields are given in Tables 1-3.

Reaction of triethylchlorosilane with alcohols. Reaction is effected in a three-necked flask with gas-tight stirrer, a reflux condenser fitted with a calcium chloride tube, and dropping funnel. A 50% ether solution of the alcohol, plus the pyridine, is placed in the flask, and the triethylchlorosilane mixed with an equal volume of ether is added with vigorous

TABLE 1

Dehydrocondensation of triethylsilane with saturated primary alcohols $R-CH_2CH_2CH_2OH$

R	Amounts of reactants					Reaction tempera-ture, °C	Reaction time, hr	Yield	
	Alcohol		Triethylsilane		0.1 M H_2PtCl_6, ml				
	g	mole	g	mole*				g	%
H	5.0	0.083	8.7	0.075	0.03	20	16	11.9	90.7
C_6H_5	6.8	0.05	5.8	0.05	0.03	70	0.5	9.1	73.4
2-furyl	6.3	0.05	5.8	0.05	0.03	80	3	10.9	90.8
$(C_2H_5)_3Si$	8.7	0.05	5.8	0.05	0.03	50	1	11.9	82.6

* After exothermic period.

stirring and ice cooling. The reaction mixture is refluxed on a steam bath, and when reaction is complete, the precipitate of pyridine hydrochloride is filtered off and washed with ether. After distilling off the ether the reaction products are separated by vacuum distillation. Tables 3 and 4 give the quantities of starting reactants, reaction conditions, and product yields.

Reaction of triethylsilane with propargyl alcohol. 5.6 g (0.1 mole) propargyl alcohol are added to 11.6 g (0.1 mole) triethylsilane and 0.04 ml of a 0.1 M solution of $H_2PtCl_6 \cdot 6H_2O$ in isopropanol. The reaction mixture is heated 3 hr at 70-80°, then 3 hr at 120°. Vacuum fractionation gives 13.8 g (80%) 3-triethylsilylprop-2-ene-1-ol boiling 84-85°/2 mm, and 1.9 g (13.3%) triethyl-3-triethylsilylprop-2-eneoxysilane boiling 119-122°(2 mm).

* Allyl alcohol and triethylsilane are added dropwise simultaneously.

Synthesis of 1-(2-furyl)-4-(triethylsilyl)butan-1-ol. 4.8 g (0.2 g-at) magnesium and 50 ml dry ether are placed in a three-necked round-bottomed flask fitted with reflux condenser and calcium chloride tube, gas-tight mechanical stirrer, and dropping funnel. A small crystal of iodine and 1 ml ethyl iodide is added, followed by 38.5 g (0.2 mole) 3-chloropropylethylsilane in 40 ml ether; which is added dropwise. The reaction mixture is stirred vigorously and refluxed on a steam bath for 3 hr. A solution of 14.4 g furfural (0.15 mole) in 25 ml ether is added, with ice cooling, to the resultant solution of 3-(triethylsilyl)propyl magnesium chloride. Next day the reaction mixture is refluxed on a steam bath for 4 hr, and then decomposed with 5% acetic acid. The ether layer is neutralized with soda, and dried over $MgSO_4$. The ether is distilled off, and the residue vacuum-distilled. Yield: 14.2 g (37.2%) of 1-(2-furyl)-4-(triethylsilyl)butan-1-ol boiling at 124°(1 mm).

TABLE 2

Reaction of triethylsilane with unsaturated primary alcohols R–CH=CHCH$_2$OH

R	Amounts of reactants: Alcohol, g	Alcohol, mole	Triethylsilane, g	Triethylsilane, mole	0,1 M H_2PtCl_6, ml	Reaction temperature, °C	Reaction time, hr	Yield, g	Yield, %
H	18,0	0,31	34,8	0,3	0,1	to 60	1	38,0*	75,4
C_6H_5	13,2	0,098	11,6	0,1	0,05	to 60	1	20,7	84,6
C_6H_5	6,7	0,05	5,8	0,05	0,02**	100—105	17,5	3,8	30,3
2-furyl	12,4	0,1	11,6	0,1	0,5	to 80	2	11,8	49,6
2-furyl	6,2	0,05	5,8	0,05	0,02**	100—105	15	1,5	12,6
$(C_2H_6)_3Si$	8,6	0,05	5,8	0,05	0,03	100—105	8	5,3	37

* 6 g product resulting from reaction with 2 molecules of $(C_2H_5)_3SiH$ also isolated.
** Amount of sodium in g.

TABLE 3

Reactions of triethylsilane and triethylchlorosilane with secondary alcohols R–CH$_2$CHOH–R'

R	R'	Alcohol, g	Alcohol, mole	Triethyl silane, g	Triethyl silane, mole	0,1 M H_2PtCl_6, ml	Pyridine, g	Pyridine, mole	Reaction temperature, °C	Reaction time, hr	Yield, g	Yield, %
Reaction with triethylsilane												
$(C_2H_5)_3SiCH_2CH_2$	2-furyl	5,0	0,02	2,3	0,02	0,02			100	10	2,4	32,6
CH_2=CH	2-furyl	13,8	0,1	11,6	0,1	0,1			20—25	16	2,8	11
									120	5	4,5*	24,4
CH_2=CH	CH_3	4,3	0,05	5,8	0,05	0,03			20—25	16	2,8	28
									90—100	11	2,9*	36,4
CH_3CH_2	CH_3	4,4	0,05	5,8	0,05	0,04			100	6	5,8	57,4
Reaction with triethylchlorosilane												
CH_2=CH	2-furyl	6,9	0,05	7,5	0,05		4,5	0,057	20—25	16	6,1	48,4
									35—40	5		
CH_2=CH	CH_3	3,5	0,04	5,7	0,038		3,5	0,044	20—25	16	4,3	56,6
									35—40	3		

* Product of reaction with 2 molecules of $(C_2H_5)_3SiH$.

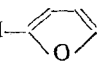
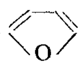
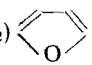
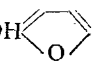
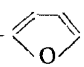
TABLE 4

Reaction of triethylchlorosilane with unsaturated primary alcohols R–CH=CHCH$_2$OH

R	Amounts of reactants: Alcohol, g	Alcohol, mole	Triethylsilane, g	Triethylsilane, mole	Pyridine, g	Pyridine, mole	Reaction time, hr	Yield, g	Yield, %
H	3,1	0,053	7,5	0,05	4,5	0,057	3	6,2	72
C_6H_5	6,7	0,05	7,5	0,05	4,5	0,057	6	9,8	79
2-furyl	6,2	0.05	7,5	0,05	4,5	0,057	3	9,0	75,5
$(C_2H_5)_3Si$	4,5	0,026	3,7	0.025	2,2	0,028	3	5,8	81

TABLE 5

Triethylsilyl ethers and triethylsilyl derivatives of alcohols

Compound	bp, °C (pressure, mm)	n_D^{20}	d_4^{20}	MR_D		Molecular formula	Si, %	
				Found	Calculated		Found	Calculated
$(C_2H_5)_3SiOCH_2CH{=}CH-$ 	124(4)	1.4934	0.9565	72.49	70.58	$C_{13}H_{22}O_2Si$	11.72; 11.80	11.78
$(C_2H_5)_3SiOCH_2CH_2CH_2-$ 	112—113(3)	1.4581	0.9295	70.59	71.05	$C_{13}H_{24}O_2Si$	11.40; 11.43	11.68
$(C_2H_5)_3SiOCH(CH_2CH{=}CH_2)$ 	110—111(5.5)	1.4644	0.9311	74.86	75.21	$C_{14}H_{24}O_2Si$	11.04; 11.09	11.13
$(C_2H_5)_3SiCH_2CH_2CH_2CHOH$ 	124(1)	1.4810	0.9465	76.50	76.47	$C_{14}H_{26}O_2Si$	11.13; 11.23	11.04
$(C_2H_5)_3Si(CH_2)_3[(C_2H_5)_3SiO]CH-$ 	157—159(2)	1.4706	0.9129	112.77	112.73	$C_{20}H_{40}O_2Si_2$	15.02; 15.09	15.23
$(C_2H_5)_3SiOCH_2CH{=}CHC_6H_5$	141—141.5(3.5)	1.5120	0.9391	79.38	77.75	$C_{15}H_{24}OSi$	11.28; 11.28	11.30
$(C_2H_5)_3SiOCH_2CH_2CH_2C_6H_5$	129,5—130(3.5)	1.4821	0.9140	78.13	78.22	$C_{15}H_{26}OSi$	11.11; 11.16	11.21
$(C_2H_5)_3SiOCH_2CH{=}CH_2$*	45(4)	1.4290	0.8332	53.32	53.36	$C_9H_{20}OSi$	16.21; 16.23	16.30
$(C_2H_5)_3SiOCH(CH_3)CH_2CH{=}CH_2$	66(4)	1.4328	0.8267	62.79	62.62	$C_{11}H_{24}OSi$	13.83; 13.91	14.02
$(C_2H_5)_3SiOCH(CH_3)CH_2CH_2CH_3$	54(2)	1.4247	0.8212	62.99	63.09	$C_{11}H_{26}OSi$	13.82; 13.84	13.88
$(C_2H_5)_3SiOCH_2CH{=}CHSi(C_2H_5)_3$	115(1.5)	1.4550	0.8603	90.39	90.41	$C_{15}H_{34}OSi_2$	19.36; 19.41	19.46
$(C_2H_5)_3SiOCH_2CH_2CH_2Si(C_2H_5)_3$	124,5—125.5(2.5)	1.4479	0.8502	90.86	90.88	$C_{15}H_{36}OSi_2$	19.29; 19.31	19.33
$(C_2H_5)_3SiOCH(CH_3)(CH_2)_3Si(C_2H_5)_3$	132—134(1.5)	1.4496	0.8517	100.35	100.14	$C_{17}H_{40}OSi_2$	17.59; 17.63	17.74
$(C_2H_5)_3SiCH{=}CHCH_2OH$	84—85(2)	1.4670	0.8852	54.02	54.15	$C_9H_{20}OSi$	16.20; 16.26	16.30
$(C_2H_5)_3SiCH_2CH_2CH_2OH$**	102,5—103.5(7)	1.4550	0.8665	54.59	54.62	$C_9H_{22}OSi$	16.02; 16.08	16.11
$(C_2H_5)_3SiCH_2CH_2CH_2Cl$	69(2.5)	1.4560	0.9125	57.44	57.91	$C_9H_{21}ClSi$	14.36; 14.40	14.57
$C_2H_5SiCl_2CH_2CH_2CH_2OOCCH_3$	92(3)	1.4504	1.1377	54.18	54.34	$C_7H_{14}Cl_2O_2Si$	12.11; 12.20***	12,25

* Literature values: bp 87-90(4); n_D^{20} 1.4348; d_4^{20} 0.8488[16]; (data wrong); bp 44.5(3.5); n_D^{20} 1.4278; d_4^{20} 0.8332[27].

** Literature values: bp 102-104(7); n_D^{20} 1.4421; d_4^{20} 0.8474[16]; bp 80-81(3); n_4^{20} 0.8565[28].

*** Found: Cl 31.26; 31.19%, calculated: 30.94%.

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