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

E. A. Lukevits and M. G. Voronkov

When triethylsilane is reacted with unsaturated primary alcohols such as allyl, cinnamic, and furylallyl alcohols, in the presence of H$_2$PtCl$_6$, 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$_2$PtCl$_6$ hydrosilanes readily undergo dehydrocondensation with organic compounds containing a hydroxyl group (alcohols, phenols, carboxylic acids) and with water [1-13] according to the equation

\[ \text{Si-} + \text{H-O-R} \rightarrow \text{Si-} + \text{H}_2 + \text{R-O-}. \]

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

\[ \text{Si-} + \text{H} \rightarrow \text{Si-} + \text{Si-}. \]

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$_2$PtCl$_6$ 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

\[ \text{Si-} + \text{H} \rightarrow \text{Si-} + \text{Si-}. \]

A patent [17] states that in the presence of Pt/γ-Al$_2$O$_3$, pentamethyldisiloxane 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$_2$PtCl$_6$ • 6H$_2$O 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:

\[ \text{CH}_2=\text{CHCH}_2\text{OH} + \text{HSi(C}_2\text{H}_3)_3 \rightarrow \text{CH}_2=\text{CHCH}_2\text{OSi(C}_2\text{H}_3)_3 + \text{H}_2. \]

(1)

Its physical constants are the same as those of triethyloxysilane, 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 triethyloxysilane, or by hydrosilylation of allyl alcohol with subsequent dehydrocondensation of the resultant 3-triethyloxysilopropan-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 triethyloxysilane. 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:

\[ \text{(C}_2\text{H}_3)_3\text{SiH} + \text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_5\text{CH}_2\text{OH} \rightarrow \text{(C}_2\text{H}_3)_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{OH} \]

\[ \text{(C}_2\text{H}_3)_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{OH} + \text{HSi(C}_2\text{H}_3)_3 \rightarrow \text{(C}_2\text{H}_3)_3\text{Si(CH}_2\text{)}_3\text{OSi(C}_2\text{H}_3)_3 + \text{H}_2. \]

(II)
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 H₂PtCl₆ · 6H₂O, 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 H₂PtCl₆ · 6H₂O leads to dehydrocondensation:

\[ RCH=CHCH_{2}OH + \text{HSi(C}_2\text{H}_5\text{)}_3 \rightarrow RCH=CHCH_{2}OSi(C}_2\text{H}_5\text{)}_3 + \text{H}_2, \]

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:

\[ \text{CsH}_7\text{N} + \text{RCH=CHCH}_{2}\text{OH} + \text{CISi(C}_2\text{H}_5\text{)}_3 \rightarrow \text{RCH=CHCH}_{2}\text{OSi(C}_2\text{H}_5\text{)}_3 + \text{CsH}_7\text{N} \cdot \text{HCl} \]

\[ \text{H}_2\text{PtCl}_6 \rightarrow \text{RCH}_2\text{CH}_{2}\text{CH}_{2}\text{OH} + \text{HSi(C}_2\text{H}_5\text{)}_3 \rightarrow \text{RCH}_2\text{CH}_{2}\text{CH}_{2}\text{OSi(C}_2\text{H}_5\text{)}_3 + \text{H}_2, \]

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:

\[ (\text{C}_2\text{H}_5\text{)}_3\text{SiH} + \text{CH} = \text{CHCH}_{2}\text{OH} \rightarrow (\text{C}_2\text{H}_5\text{)}_3\text{SiCH} = \text{CHCH}_{2}\text{OH}, \]

80%

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

\[ (\text{C}_2\text{H}_5\text{)}_3\text{SiCH} = \text{CHCH}_{2}\text{OH} + \text{HSi(C}_2\text{H}_5\text{)}_3 \rightarrow (\text{C}_2\text{H}_5\text{)}_3\text{SiCH} = \text{CHCH}_{2}\text{OSi(C}_2\text{H}_5\text{)}_3 + \text{H}_2, \]

13%

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 much 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 H₂PtCl₆ · 6H₂O. 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 H₂PtCl₆ · 6H₂O 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-oxyisilane was obtained by reacting 2-furylallylcarbinol with triethylchlorosilane in the presence of pyridine:

\[ \text{CHO} + \text{CH}_2\text{CH} = \text{CH}_{2} + \text{ClSi(C}_2\text{H}_5\text{)}_3 \rightarrow \text{CHOHCH}_{2}\text{CH} = \text{CH}_{2} + \text{C}_6\text{H}_5\text{N} \cdot \text{HCl} \]

\[ \text{SiO} \]

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

\[ \text{CHO} + \text{ClMg(C}_2\text{H}_5\text{)}_3 \text{Si(C}_2\text{H}_5\text{)}_3 \rightarrow \text{CH(OH)(CH}_2\text{)}_3\text{Si(C}_2\text{H}_5\text{)}_3 + \text{Mg(OH)}\text{Cl}, \]

117