SYNTHESIS AND REACTIONS OF OXYGEN-CONTAINING ORGANOSILICON COMPOUNDS

COMMUNICATION 1. SYNTHESIS OF ORGANOSILICON ACETALS

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Oxygen-containing organosilicon compounds, such as silanols of general formula

\[ R \text{SiOH} \quad (R = \text{alkyl or aryl}) \]

are of great theoretical interest. There are great prospects for development in organic chemistry along the line of the unification of organic and organosilicon syntheses. The authors of this paper have undertaken the task of working out new syntheses of organosilicon compounds.

It has been shown by the work of Andrianov [1] and others [2] that organosilicon compounds have certain peculiar properties. It is well known, for example, that tertiary alcohols are readily dehydrated to unsaturated hydrocarbons, whereas trialkylsilanols, on dehydration, give stable siloxane dimers:

\[ R \text{Si} \text{OH} + \text{H} \text{O} \rightarrow R \text{Si} \text{O} \text{Si} \text{Si} \text{OH} + \text{H} \text{O} \]

We now describe a new synthesis of oxygen-containing organosilicon compounds based on the reaction of vinyl ethers with silanols. In the course of this work we have established that the reaction of alkyl vinyl ethers with trialkylsilanols proceeds similarly to the corresponding reaction with organic tertiary alcohols and may be represented by the equation:

\[ R \text{SiOH} + \text{CH}_2=\text{CH} \text{OR}' \rightarrow \text{CH}_3=\text{CH} \text{OR'} \text{OSiR} \]

We have studied methods for the preparation of the following acetals:

\[ \text{CH}_3=\text{CH} \text{OSi(C}_2\text{H}_5)_3 \quad \text{and} \quad \text{CH}_3=\text{CH} \text{OSi(C}_3\text{H}_7)_3 \]

Addition of trialkylsilanols to vinyl ethers proceeds fairly readily in presence of traces of 30% hydrochloric acid, the procedure being that which has been developed for the synthesis of acetals of organic alcohols [3]. We have in this way prepared and characterized two unsymmetrical acetals: the butyl triethylsilyl and the isobutyl triethylsilyl acetals of acetaldehyde. The structures of the organosilicon acetals obtained were proved by the products of their hydrolysis, which proceeds according to the equation:

\[ \text{CH}_3=\text{CH} \text{OSi(C}_2\text{H}_5)_3 + \text{HOH} \rightarrow \text{R'OH} + \text{CH}_3\text{C} \text{OH} + (\text{C}_2\text{H}_5)_3\text{SiOH} \]
EXPERIMENTAL

1. Synthesis of Acetaldehyde Butyl Triethylsilyl Acetal

\[ \text{CH}_2 = \text{CHOCH}_3 + (\text{C}_2\text{H}_5)_3\text{SiOH} \rightarrow \text{CH}_2\text{CH}_3 + \text{OSi}(\text{C}_2\text{H}_5)_3 \]

To a cold (room temperature) mixture of 33 g (0.25 mole) of triethylsilanol (b.p. 80°/30 mm; d\text{\textsubscript{20}} 0.8652; n\text{\textsubscript{D14}} 1.4332) and 25 g (0.25 mole) of butyl vinyl ether (b.p. 93°-94°; d\text{\textsubscript{20}} 0.7790; n\text{\textsubscript{D14}} 1.4020) 0.02 ml of 30% hydrochloric acid was added, and the temperature rose to 48°. After one hour the contents of the flask were heated under reflux in a water bath at 80-93° for one hour, and they were then set aside overnight. On the next day the reaction mixture was neutralized and dried with pepsatum carbon. The potassium carbonate was then filtered off, and the filtrate was distilled at atmospheric pressure, the following fractions being obtained:

<table>
<thead>
<tr>
<th>Fraction</th>
<th>B.p., up to 213°</th>
<th>g</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td></td>
<td>8</td>
</tr>
<tr>
<td>II</td>
<td>214-215°</td>
<td>14 g; n\text{\textsubscript{D15}} 1.4258</td>
</tr>
<tr>
<td>III</td>
<td>217-218°</td>
<td>22 g; n\text{\textsubscript{D15}} 1.4274</td>
</tr>
<tr>
<td>Residue</td>
<td></td>
<td>4 g</td>
</tr>
</tbody>
</table>

Fractions II and III were united and refractionated, yielding 32 g of a product boiling at 82-83°/9 mm; yield 55.17% on the amount of butyl vinyl ether taken. This substance had the following constants: d\text{\textsubscript{20}} 0.8574; n\text{\textsubscript{D14}} 1.4271; found MR 69.49; calculated for C\textsubscript{10}H\textsubscript{24}SiO\textsubscript{2} MR 69.85.

From the results obtained it follows that the substance of b.p. 82-83°/9 mm was acetaldehyde butyl triethylsilyl acetal. It was a clear oily liquid having an ethereal odor; it did not change in storage.

2. Hydrolysis of the Butyl Triethylsilyl Acetal

\[ \text{CH}_2\text{CH}_3 + \text{OH} \rightarrow \text{C}_4\text{H}_9\text{OH} + \text{CH}_3\text{C} = \text{CH}_2 + \text{OSi}(\text{C}_2\text{H}_5)_3 \]

Acetaldehyde was estimated in the products of the hydrolysis of the unsymmetrical organosilicon acetal by the bisulfite method. It was found that hydrolysis of the acetal by treatment with 2% sulfuric acid at 60° for 12 hours did not go well, and in further work the hydrolysis was carried out in a boiling water bath in presence of 5% sulfuric acid.

The acetal (0.3213 g) was heated with 50 ml of 5% sulfuric acid in a sealed tube for six hours. The contents of the tube were then transferred to a 200-ml measuring flask and made up to volume with distilled water. Analysis by the bisulfite method gave 86.39% of acetaldehyde (of the theoretical amount). A parallel experiment by the same method (0.4391 g of acetal) gave 84.28% of acetaldehyde. Towards the end of the hydrolysis process, an oily layer formed on the surface of the solution; this was evidently one of the hydrolysis products. The hydrolysis results show that the substance of b.p. 82-83°/9 mm was the butyl triethylsilyl acetal. It should be noted that the described hydrolysis conditions do not yield quantitative results.

3. Synthesis of Acetaldehyde Isobutyl Triethylsilyl Acetal

\[ \text{CH}_3 = \text{CHOCH}_3 + (\text{C}_2\text{H}_5)_3\text{SiOH} \rightarrow \text{CH}_3\text{CH} = \text{CH}_2 + \text{OSi}(\text{C}_2\text{H}_5)_3 \]

The conditions of the synthesis were similar to those of the preceding experiment. A mixture of 33 g (0.25 mole) of triethylsilanol and 25 g (0.25 mole) of isobutyl vinyl ether (b.p. 83°; n\text{\textsubscript{D14}} 1.3986; d\text{\textsubscript{20}} 0.7880) was placed in a 150-ml round-bottomed flask fitted with reflux condenser, thermometer, and mechanical stirrer. The mixture was constantly stirred at room temperature, and 0.02 ml of 30% hydrochloric acid was added, when the temperature rose to 45°. Stirring was continued for 80 minutes, and the temperature was raised to 84°. The mixture was set aside overnight, and on the next day it was dried with calcined potassium carbonate, and distilled, the following fractions being obtained:

<table>
<thead>
<tr>
<th>Fraction</th>
<th>B.p., up to 200°</th>
<th>g</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td></td>
<td>13 g</td>
</tr>
<tr>
<td>II</td>
<td>210-216°</td>
<td>38 g</td>
</tr>
<tr>
<td>Residue</td>
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<td>4 g</td>
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