REACTION FOR EXPANSION OF SILICOCARBON HETEROCYCLES UNDER THE INFLUENCE OF NUCLEOPHILIC REAGENTS

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The reaction for expansion of silicocarbon heterocycles containing one silicon atom was already previously reported by us on the example of chloromethyl derivatives of the type

\[
\begin{align*}
\text{CH}_2 & \quad \text{CH}_2\text{Cl} \\
\text{Si} & \quad \text{X} \\
\text{CH}_3 & \quad \text{CH}_3
\end{align*}
\]

\[(n = 2, 3; \text{X} = \text{Cl, CH}_3)\] by treatment with electrophilic reagents \((\text{AlCl}_3)\) [1-4]. It was shown that of the four possible directions the reaction proceeds mainly in direction (1) (to the extent of 80 and 90\%, respectively).

\[
\begin{align*}
\text{CH}_2 & \quad \text{CL} \\
\text{Si} & \quad \text{X} \\
\text{CH}_2 & \quad \text{CH}_3
\end{align*}
\]

\[(\text{CH}_2)_n\] (1)

In the case where \(\text{X} = \text{Cl}\) it is possible for the reaction to proceed according to scheme (2) to the extent of 10-30\%. Ethylsilacycloalkanes [reaction (3)], the formation of which is possible in view of the data given in [5], were not found in the reaction products. Polymerization [reaction (4) with \(n = 2\)], a property that is characteristic for 1-silacyclopentane derivatives, also fails to take place. Recently some Japanese authors found that disilanes of the type \((\text{CH}_3)_3\text{SiSiCH}_2\text{Cl}\) undergo rearrangement with the formation of \(\text{CH}_3\) bridged compounds under the influence of nucleophilic reagents under drastic conditions [6].

We found that the reaction for the expansion of silicocarbon heterocycles of the above indicated type can also take place under the influence of nucleophilic reagents (sodium methylate, sodium or potassium hydroxide in methyl alcohol). The same as in the first case, the reaction is exothermic and proceeds at high speed.

\[
\begin{align*}
\text{Cl}_2\text{SiCH}_3 & \quad \text{abs} \quad \text{MOR} \quad \text{NaCl} \quad \text{OH} \\
\text{CH}_3 & \quad \text{Si} \quad \text{Na} \quad \text{M} = \text{Na, K} \quad \text{R} = \text{CH}_3, \text{H}
\end{align*}
\]

(1)

The nucleophilic reagent was taken in slight excess. The formation of disiloxane (I) during reaction is apparently explained by the catalytic action of the reagent.

\[ \text{Si} \quad \text{OCH}_3 \quad \underset{\text{MOR}}{\xrightarrow{\text{H}^+}} \quad \text{Si} \quad \text{OCH}_3 \quad \text{Si} \quad \text{OCH}_3 \quad \text{CH}_3 \text{OCH}_3 \]

In the case of 1-chloromethyl-1-chloro-1-silacyclopentane the reaction product was 1,1-dimethyl-1-silacyclohexane, from which cyclic siloxanes were obtained by acid hydrolysis and rearrangement as described in [7].

\[ \text{Si} \quad \text{CHCl}_3 \quad \underset{\text{MOR, abs. CH}_3\text{OH}}{\xrightarrow{\text{H}^+}} \quad \text{Si} \quad \text{OCH}_3 \quad \text{H}_2\text{O} \quad \text{KOH} \quad \text{Si} \quad \text{OCH}_3 \quad \text{Si} \quad \text{OCH}_3 \quad \text{CH}_3 \text{OCH}_3 \]

The progress of reaction (3) could also be expected when the chloromethyl derivatives of 1-silacyclopentane are rearranged under the influence of nucleophilic reagents. However, spectral analysis of the disiloxane obtained according to reaction (5) confirmed the structure assigned to it, namely \[ \text{Si} \quad \text{OCH}_3 \quad \text{CH}_3 \text{OCH}_3 \]. This is evidenced by the absence of a doublet of absorption bands at 1030-1020 cm\(^{-1}\), characteristic for derivatives having the 1-silacyclopentane ring [8] (including the siloxane \[ \text{Si} \quad \text{OCH}_3 \quad \text{CH}_3 \text{OCH}_3 \]), in the infrared spectra of the compound. Frequencies at 970, 1237 and 1420 cm\(^{-1}\), which characterize the Si – C\(_2\)H\(_5\) group, were also not detected.

Proof that the reaction proceeds according to scheme (5) is the complete identity of the infrared spectra of compound (I) and the product obtained by the reaction:

\[ \text{Si} \quad \text{CH}_3 \quad \underset{\text{CH}_3\text{OCH}_3}{\xrightarrow{\text{MOR}}} \quad \text{Si} \quad \text{OCH}_3 \quad \text{CH}_3 \text{OCH}_3 \]

As a result, on the basis of the data obtained by us it is possible to conclude that the reaction for the expansion of a five-membered silicocarbon heterocycle to a six-membered ring is the main direction of the transformation under the influence of nucleophilic reagents. Besides the product expected according to reaction (3), we also failed to detect substantial amounts of 1-silacyclopentane derivatives in the reaction mixture, which could have been formed either by cleavage of the chloromethyl group or by ordinary nucleophilic substitution. It is interesting to mention that in harmony with the data given in [9, 10], in the reliability of which we became convinced by running additional experiments, chloromethyltrialkylsilanes (for example, trimethylchloromethylsilane) react with ethoxide ion by the nucleophilic substitution scheme, and cleavage of the chloromethyl radical occurs as a side reaction.

\[ \text{R}_3\text{SiCH}_2\text{Cl} \quad \underset{\text{C}_3\text{H}_5\text{O}^\ominus}{\Rightarrow} \quad \text{R}_3\text{SiOC}_2\text{H}_5 \quad (86\%) \]

\[ \text{R}_3\text{SiCH}_2\text{Cl} \quad \underset{\text{C}_3\text{H}_5\text{O}^\ominus}{\Rightarrow} \quad \text{R}_3\text{SOCC}_2\text{H}_5 \quad (44\%) \]

As a result, the transformation discovered by us is specific for silacycloalkanes.

**EXPERIMENTAL**

I. Reaction of 1-chloromethyl-1-methyl-1-silacyclopentane (II) with sodium methylete (III). Into a 100-ml round-bottomed flask were charged 30 ml of absolute methanol and 2.8 g of sodium metal. At the end of reaction, 14.8 g of (II) was added gradually to the formed solution of (III) and the mixture was heated up to reflux. The burner was removed just as soon as the boiling point was reached and the reaction continued spontaneously. When the exothermic reaction had ceased the mixture was heated an additional 15 min. The obtained precipitate was separated, the solvent was distilled off, and the mixture was fractionally