DIRECT SYNTHESIS OF 1,1-DICHLOROSILYLCYCLOPENTANE

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All known cyclic organosilicon compounds in which the ring is made up of carbon atoms and a silicon atom have been prepared previously only by the organometallic method of synthesis [1-4]. We recently reported [5] that the reactions of 3,4-dichloro-1-butene and of 1,4-dichloro-2-butene with copper-silicon alloy result in the formation of 1,1-dichlorosilacyclopentane-3-ene. It was of undoubted interest to study also the behavior of 1,4-dichlorobutane in the direct synthesis, because it would be expected that in this case also ring-closure would occur. Such behavior, however, would be contrary to the already existing data of English and co-workers [6], according to which the reaction of 1,4-dichlorobutane with silicon gives only 1,1,1,6,6,6-hexachloro-1,6-disilahexane in very low yield.

We were doubtful about these data, and we undertook an investigation in which we established the following: the main product of the reaction of 1,4-dichlorobutane with silicon is 1,1-dichlorosilacyclopentane (I). The yield of this compound (its content in the condensate) was 30%. Another monosilane, 3-butenyldichlorosilane (II), is evidently formed by the elimination of hydrogen chloride from 1,4-dichlorobutane and reaction of the product, 4-chloro-1-butene, with silicon. Proof of this was provided by our detection of 4-chloro-1-butene in the reaction mixture. Apart from these monosilanes, in the reaction of 1,4-dichlorobutane with silicon we isolated the disilicon compounds 1,1,1,6,6-pentachloro-1,6-disilahexane (III) and 1,1,1,6,6,6-hexachloro-1,6-disilahexane (IV). To confirm the correctness of the structures of the chlorosilanes they were converted into silahydrocarbons with the aid of methylmagnesium chloride, and these were then analyzed.

\[
\begin{align*}
\text{CH}_2\text{=CH}_2\text{Cl} + \text{SiCl}_4 & \xrightarrow{300\pm10^\circ} \text{CH}_2\text{=CH}_2\text{SiCl}_3 \quad \text{(I)} \\
\text{CH}_2\text{=CH}_2\text{Cl} & \xrightarrow{300\pm10^\circ} \text{CH}_2\text{=CH}_2\text{SiCl}_3 + \text{HCl}_{2}\text{SiCH}_2\text{CH}_2\text{CH}_3\text{CH} = \text{CH}_2 \\
\text{(II)} \\
+ \text{HCl}_{2}\text{Si(CH}_3)_2\text{SiCl}_3 + \text{Cl}_3\text{Si(CH}_3)_2\text{SiCl}_3 \\
\text{(III)} (\text{IV})
\end{align*}
\]

We studied some chemical properties of 1,1-dichlorosilacyclopentane. Thus, in its chlorination with sulfonyl chloride, hydrogen on the β-carbon atom is replaced by chlorine. In the reaction of 1,1,3-trichlorosilacyclopentane (V) with methylmagnesium chloride, replacement of chlorine by methyl groups is accompanied by decyclization at the Si-C bond, or so-called β-decomposition [7]:

\[
\begin{align*}
\text{CH}_2\text{=CH}_2\text{SiCl}_3 & \xrightarrow{\text{SO}_2\text{Cl}_2} \text{CH}_2\text{=CH}_2\text{SiCl}_3 \quad \text{Cl} \quad \text{(I)} \\
\text{CH}_2\text{=CH}_2\text{SiCl}_3 & \xrightarrow{\text{CH}_3\text{MgCl}} \text{CH}_2\text{=CH}_2\text{SiCl}_3 \quad \text{(V)} \\
\text{CH}_2\text{=CH}_2\text{SiCl}_3 + \text{CH}_3\text{MgCl} & \xrightarrow{\text{Cl}} \text{CH}_3\text{SiCH}_2\text{CH}_2\text{CH} = \text{CH}_2 \\
\text{(VI)}
\end{align*}
\]

The properties of the 3-butenyldichlorosilane (VI) formed by decyclization were found to be identical with those of the same substance as prepared by us previously by the Grignard-Wurtz reaction from trichloro(chloromethyl) silane and allyl bromide [8]. In the hydrolysis of 1,1-dichlorosilacyclopentane with aqueous alkali under the conditions used for the conversion of dichlorodiethylsilane into the corresponding diol [9] we isolated only a condensation product, a poly(tetramethylenesiloxane). The reactions of 1,1-dichlorosilacyclopentane with allylmagnesium

* Prefix sila- = silyl or silico-, indicates presence of a single silicon atom.*
bromide and with acetic anhydride went in the usual way, i.e. the chlorine atoms were replaced by allyl and acetoxy, respectively.

\[
\begin{align*}
&(CH_2)_3Si(CH_2CH\equiv)CH_2CH\equivCH(CH_2CHBr)CH_2CH\equivCH-MgBr & \text{CH}_3CH=CHCH_2MgBr & \text{VII} \\
&(CH_2)_4SiCl_2(\text{CH}_3CO)O & \text{CH}_3CO(\text{CH}_2)Si(\text{OCOCH}_3)_2 & \text{VIII}
\end{align*}
\]

Hydrogen bromide added vigorously to 1,1-diallylsilacyclopentane (VII) at -10°. The resulting dibromo compound (CH_2)_3Si(CH_2CHBrCH_2)_2 was unstable; when heated, it underwent β-decomposition, with elimination of propene and formation of 1,1-dibromosilacyclopentane.

**EXPERIMENTAL**

**Direct Synthesis.** 1,4-Dichlorobutane (800 g) was passed at 23 g/hour through a tube filled with Si-Cu alloy at 300 ± 10°. Fractionation of 730 g of reaction mixture collected from the condenser gave: trichlorosilane, 38 g (5.3%); silicon tetrachloride, 44.5 g (6.1%); 4-chloro-1-butene, 24.3 g (3.3%); b.p. 74-75°, nD^20 1.4226 (the literature [10] gives b.p. 74.5-75.5°, nD^20 1.4233) the Raman spectrum of this compound contained frequencies characteristic of the CH=CH_2 group; 3-butenyldichlorosilane (II), 36.5 g (5%), b.p. 125.5-127° (743 mm); nD^20 1.4446, d_4^20 1.0724; 1,1-dichlorosilacyclopentane (I), 217 g (29.7%), b.p. 139.5° (732 mm); nD^20 1.4645; d_4^20 1.1768; found Mr 36.40; calculated Mr 36.67 (the literature [11] gives m.p. 140-141° (752 mm), nD^20 1.4644, d_4^20 1.1798, m.p. 141° nD^20 1.4651; 1,1,1,6,6-pentachloro-1,6-disilahexane (III), 41 g (5.7%), b.p. 230° (729 mm); nD^20 1.4792; d_4^20 1.3516; found Mr 65.86; calculated Mr 65.47.

Found %: C 17.52; H 3.09; Si 19.64; C_4H_8Si_2C_1_8. Calculated %: C 16.53; H 3.12; Si 19.33.

1,1,6,6,6-hexachloro-1,6-disilahexane (IV), 44.5 g (6.1%), b.p. 250° (738 mm); m.p. 26.5-27°, nD^20 1.4722; d_4^20 1.3823, found Mr 65.86; calculated Mr 65.47.

Found %: C 15.12; H 2.55; Si 18.00; C_4H_14Si_2C_1_6. Calculated %: C 14.78; H 2.48; Si 17.28.

The residue amounted to 134 g (18.4%). In the calculation of yields the intermediate fractions were not taken into account. Increase in the rate of passage of 1,4-dichlorobutane from 23 to 30 g/hour reduced the yield of 1,1-dichlorosilacyclopentane from 29.7% to 25%.

**Methylation of the Products of Direct Synthesis (IV)-(VII).** The methylation was carried out with methylmagnesium chloride, which was taken in excess. The procedure was almost the same in all cases. Over a period of 40 minutes, 31 g (0.2 mole) of 1,1-dichlorosilacyclopentane was added to an ethereal solution of CH_3MgCl prepared from 14.6 g (0.6 mole) of magnesium and methyl chloride. The reaction mixture was heated in a water bath for seven hours, and was then treated with water and 5% hydrochloric acid. By distillation we isolated from the ethereal solution 12.6 g (55%) of 1,1-dimethylsilacyclopentane; b.p. 104.5° (73 mm); nD^20 1.4340; d_4^20 0.7893.

Found %: C 63.30; H 12.22; Si 18.17; C_4H_14Si. Calculated C 63.97; H 12.35; Si 18.46.

The literature [1, 2] gives b.p. 105° (742 mm); nD^20 1.4348; d_4^20 0.7939; b.p. 107°, nD^20 1.4335; d_4^20 0.780.

From (II) we obtained 3-butenyldimethylsilane, b.p. 98.5° (735 mm); nD^20 1.4161; d_4^20 0.7292; found MR 39.33; calculated MR 39.33.

Found %: C 62.75; H 12.44; Si 24.51; C_4H_14Si. Calculated %: C 63.08; H 12.36; Si 24.56.

From (III) we obtained 2,2,7-trimethyl-2,7-disilaoctane, b.p. 182° (752 mm); nD^20 1.4341; d_4^20 0.7770; found MR 63.18; calculated MR 63.32.

Found %: C 58.97; H 12.36; Si 29.67; C_8H_18Si_2. Calculated %: C 57.35; H 12.84; Si 29.81.

From (IV) we obtained 2,2,7,7-tetramethyl-2,7-disilaoctane, b.p. 191.7° (746 mm); nD^20 1.4270; d_4^20 0.7652 (the literature [3] gives b.p. 199° (748 mm); nD^20 1.4244; d_4^20 0.763.

1,1-Diallylsilacyclopentane. Over a period of two hours 19.5 g (0.2 mole) of magnesium in ether suspension was added to a mixture consisting of 31 g (0.2 mole) of 1,1-dichlorosilacyclopentane and 72.6 g (0.6 mole) of allyl bromide. The reaction mixture was boiled for seven hours, part of the ether was distilled off, and heating was continued further for 90 minutes at 70-80°. In the usual way we isolated from the ethereal solution 16.7

* Molar refractivity.