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Abstract

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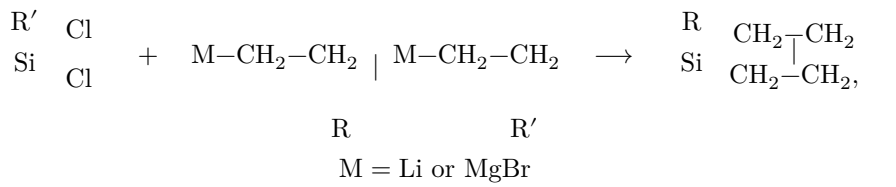
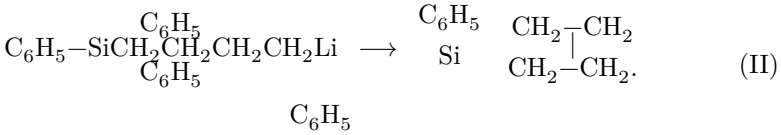
CATALYTIC REACTIONS FOR THE FORMATION OF 1,1-DIMETHYLSILICACYCLOPENTANE

For the synthesis of silicacyclopentane compounds, organometallic derivatives of tetramethylene dibromide are usually used ([1]-[3])



(I)

Wittenberg ([4]) obtained a silicacyclopentane derivative by another reaction (II), likewise through an organometallic compound



(II)

The formation of silicon-carbon five-membered rings substituted on carbon was observed in reactions of dialkyldichlorosilanes with lithium and conjugated olefins (styrene, tolane, etc.) ([5]). 1,1-Dichloro-1-silicacyclopentane was isolated from the products of the reaction of 1,4-dichlorobutane and a copper-silicon alloy ([6]).

In the present work we report previously unknown reactions for the formation of a five-membered silicon-carbon ring—1,1-dimethyl-1-silicacyclopentane. We have shown that 1-chloromethyldimethylsilyl-3-trimethylsilylpropane, under the action of catalytic amounts of aluminum chloride, is converted into 1,1-dimethylsilicacyclopentane:

$$\mathrm{ClCH_2Si(CH_3)_2CH_2CH_2CH_2Si(CH_3)_3} \xrightarrow{[\mathrm{AlCl_3}]} \begin{matrix} \mathrm{CH_3} & \mathrm{CH_2{-}CH_2} \\ \mathrm{Si} & \quad\vert \\ & \mathrm{CH_2{-}CH_2} \end{matrix} \quad \mathrm{CH_3} + \mathrm{(CH_3)_3SiCl} \qquad \text{(III)}$$

The yields of 1,1-dimethylsilicacyclopentane and trimethylchlorosilane are 38% and 41%, respectively, based on the 1-chloromethyldimethylsilyl-3-trimethylsilylpropane taken. Evidently, as a result of this reaction the trimethylene grouping

$$\equiv \mathrm{Si(CH_2)_3Si} \equiv$$

is extended to the tetramethylene grouping

$$\equiv \mathrm{Si(CH_2)_4Si} \equiv$$

and this grouping is realized in a five-membered heterocycle.

A similar phenomenon was observed by us previously ([7]) in the example of reaction (IV) of a five-membered silicon-carbon heterocycle containing a chloromethyl group and the bond system

$$\equiv \mathrm{Si(CH_2)_3Si} \equiv$$

$$\begin{matrix} \mathrm{ClCH_2} \\ \mathrm{Si} \end{matrix} \begin{matrix} \mathrm{CH_2{-}CH_2} \\ \quad\vert \\ \mathrm{CH_2{-}CH_2} \end{matrix} \mathrm{CH_3} \xrightarrow{[\mathrm{AlCl_3}]} \begin{matrix} \mathrm{Cl} \\ \mathrm{Si} \end{matrix} \begin{matrix} \mathrm{CH_2{-}CH_2} \\ \mathrm{CH_2{-}CH_2} \end{matrix} \mathrm{CH_2}. \qquad \text{(IV)}$$

$$\mathrm{CH_3}$$

In reaction (IV), the tetramethylene grouping is extended to a pentamethylene grouping and is realized in a six-membered heterocycle. It is interesting to note that, in contrast to the cyclization reaction (III), the exothermic ring-expansion reaction (IV) proceeds more vigorously, in an explosion-like manner.

The formation of 1,1-dimethyl-1-silacyclopentane was also observed by us in the interaction of 1,3-di-(trimethylsilyl)butane with aluminum chloride according to reaction (V):

$$\mathrm{(CH_3)_3SiCH_2CH_2CH_2CH_2Si(CH_3)_3} \xrightarrow{[\mathrm{AlCl_3}]} \begin{matrix} \mathrm{CH_3} & \mathrm{CH_2{-}CH_2} \\ & \backslash\ \ / \\ & \mathrm{Si} \\ & /\ \ \backslash \\ \mathrm{CH_3} & \mathrm{CH_2{-}CH_2} \end{matrix} + \mathrm{(CH_3)_4Si} + \text{condensation products} \qquad \text{(V)}$$

The yield of 1,1-dimethylsilacyclopentane was 25% based on the hexamethyldisilylbutane used. Carrying out the indicated reaction was possible only with incomplete conversion of 1,3-di-(trimethylsilyl)butane.

It is known [8] that, when this reaction is carried through to the formation of the calculated amount of tetramethylsilane, only a mixture of silicon–carbon oligomers of the type

$$\left[-SiCH_2CH_2CH_2CH_2- \begin{matrix} CH_3 \\ CH_3 \end{matrix}\right]_x$$

is formed.

Synthesis of 1-chloromethyldimethylsilyl-3-trimethylsilylpropane. As the starting product we took γ-bromopropyltrimethylsilane, obtained by the method of [9] from 3-hydroxypropyltrimethylsilane [10].

To an organomagnesium compound prepared from 163 g of 0.82 g-mol of γ-bromopropyltrimethylsilane and 50 g (2.2 g-atoms) of magnesium in 750 ml of absolute ether, 114 g (0.8 g-mol) of chloromethyldimethylchlorosilane was added while heating on a water bath. The resulting mixture was boiled for 6 hours, after which it was decomposed with water and worked up in the usual manner.

Table 1

Properties of 1,1-dimethylsilacyclopentane

Method of preparation	B.p., °C	n_D^{20}	d_4^{20}
By reaction (I) from BrMg $(CH_2)_4$MgBr + $(CH_3)_2SiCl_2$	103–104	1.4345	0.7941
By reaction (III) from 1-chloromethyldimethylsilyl-3-trimethylsilylpropane	104–104.5	1.4335	0.7935
By reaction (V) from 1,4-di-(trimethylsilyl)butane	103–105	1.4300	0.7923

By double distillation on a column under reduced pressure, 61 g (0.27 g-mol) of pure 1-chloromethyldimethylsilyl-3-trimethylsilylpropane was obtained. Yield

Fig. 1. Chromatogram of 1,1-dimethylsilacyclopentane

Figure 1: Fig. 1. Chromatogram of 1,1-dimethylsilacyclopentane

30%, b.p. 82.5-83°/9 mm, n_D^{20}–1.4470, d_4^{20}–0.8795, MR_D calculated 67.90, found 67.73. Molecular weight calculated 222; found 215 by the cryoscopic method in benzene:

$C_9H_{23}Si_2Cl$.	Found %:	Si 24.73
	Calculated %:	Si 25.2

Interaction of 1-chloromethyldimethylsilyl-3-trimethylsilylpropane with aluminum chloride. In a flask equipped with a stirrer and reflux condenser and isolated from the external atmosphere by a calcium chloride tube, 42 g (0.19 g-mol) of 1-chloromethyldimethylsilyl-3-trimethylsilylpropane and 1.33 g (0.01 g-mol) of aluminum chloride were placed. The mixture was stirred and heated with an oil bath. At a bath temperature of 180° the contents of the flask boiled; boiling continued at a bath temperature of 140°. After 0.5 hour, to bind the aluminum chloride, 3 g of ignited sodium chloride was added, after which the mixture continued to be stirred and heated for another 0.5 hour. After cooling, the liquid part was decanted from the precipitate and distilled on a column. Fraction 1. 8.5 g, b.p. 58-58.2°, n_D^{20}–1.3878, d_4^{20}–0.8586. The percentage of hydrolyzable Cl–33.5 represents trimethyl-

chlorosilane. Fraction 2. 8.2 g, b.p. 104–105.5°, n_D^{20} –1.4338; d_4^{20} –0.8167, contains traces of hydrolyzable chlorine. Raman spectrum* (Δ in cm^{-1}): 173 (1 sh); 209 (2 sh); 228 (0); 395 (6); 595 (10); 623 (1); 645 (1 sh); 668 (1 sh); 700 (1 sh); 715 (1); 752 (1); 783 (0 sh); 837 (0); 853 (4); 947 (2); 1023 (2); 1037 (1); 1127 (1); 1150 (1); 1170 (0); 1250 (2 sh); 1315 (1 sh); 1357 (0); 1410 (2 sh); 1446 (2); 2852 (7); 2897 (10 sh); 2939 (7); 2960 (5).

All frequencies, with the exception of 623, 752, 837, 1127, 1170, correspond to the spectrum of 1,1-dimethylsilacyclopentane ([11]). After treatment of the ether solution of fraction 2 with water, pure 1,1-dimethylsilacyclopentane was isolated; its constants are given in Table 1, and the chromatogram is shown in Fig. 1. Fraction 3. 15 g, b.p. 82–91°/17 mm, n_D^{20} 1.4425, d_4^{20} –0.7863. Percentage of hydrolyzable Cl 3.71. The ether solution of the substance was treated with water, after which a product was obtained with b.p. 70–80°/5 mm, n_D^{20} 1.4430. The main component of this fraction is the starting 1-chloromethyldimethylsilyl-3-trimethylsilylpropane (according to chromatographic analysis).

Fig. 1. Chromatogram of 1,1-dimethylsilacyclopentane (Ia, IIa); Ib, IIb – ether; IIc –tetramethylsilane

Synthesis of 1,4-di-(trimethylsilyl)butane. The synthesis of this product was carried out by the known procedure ([12]), but ether was used instead of tetrahydrofuran.

Yield of 1,4-di-(trimethylsilyl)butane 60%, b.p. 194–195°/atm, n_D^{20} 1.4265, d_4^{20} 0.7663. Literature data ([12]): yield 67%, b.p. 193°/732 mm, n_D^{20} –1.4260, d_4^{20} – 0.7651.

Reaction of 1,4-di-(trimethylsilyl)butane with aluminum chloride. Into a Claisen flask were placed 30 g (0.14 g-mol) of 1,4-di-(trimethylsilyl)butane and 2 g (0.014 g-mol) of aluminum chloride; the mixture was heated and the low-boiling fraction with b.p. 26–60°, n_D^{20} 1.3721, was collected in a receiver cooled with dry ice. After 8 ml of low-boiling products had distilled off, the mixture was cooled, diluted with ether, and hydrolyzed with water. The dry ether extract was combined with the low-boiling products and distilled on a rectification column: 5.2 g of tetramethylsilane with b.p. 26°, n_D^{20} 1.3590; 2 g of 1,1-dimethylsilacyclopentane (Table 1, Fig. 1, II); 16 g of unreacted 1,4-di-(trimethylsilyl)butane were obtained. In the residue there remained 4 g of a viscous oil consisting of polymeric silicon hydrocarbons ([8]).

The chromatograms shown in Figures 1 and 2 were recorded on an LKhM-5 instrument. Column with $l = 2$ m, inner diam. = 6 mm. Packing: Inza brick-

* The spectrum was obtained on an ISP-51 instrument with a medium camera. Intensities are given on a ten-point visual scale.

FID + 20% PFM, carrier gas–helium. The experimental temperature was 120°, and the carrier-gas flow rate was 40 ml/min. Control experiments showed that the retention time of tetramethylsilane was 1 min 25 sec; that of the ether, 2 min 35 sec; and that of 1,1-dimethylsilacyclopentane obtained by reaction (I) [(1)], 4 min 44 sec. In retention time, the peaks of the principal product and the very weak impurity peaks correspond exactly to the controls.

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Note: Figure translations are in progress. See original paper for figures.