SYNTHESIS OF DISILACYCLOALKANES

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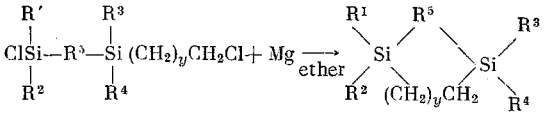
At present, a significant number of 1,3-disilacyclobutanes, obtained by different methods [1, 2], are known. As for disilacyclopentanes and higher members of the homologous series, they are represented by only several compounds, formed normally as side products in reactions of polyaddition [3] and polycondensation [4], in the reaction of Li(Na) with dialkyldichlorosilanes and ethylene in THF [5], or as a result of a multistage organometallic synthesis [6].

We have developed a general method for synthesizing disilacycloalkanes based on the intramolecular cyclization reaction of α,ω-polyfunctional organosilicon compounds, containing two types of reaction centers: Si – X (X is a halogen) and Si – R – Cl groups.

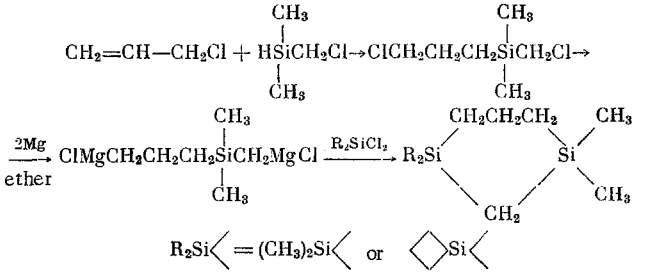


(1)

In particular, the following compounds were obtained:

Number	y	R′	R^2	R^3	R^4	R^5
1	0	Cl	Cl	CH_3	CH_3	$CH_3CH=$
2	0	Cl	Cl	CH_3	CH_3	$—CH_2—CH_2—$
3	0	Cl	Cl	CH_3	CH_3	$—(CH_2)_3—$
4	0	CH_3	CH_3	CH_3	CH_3	$—(CH_2)_3—$
5	0	Cl	CH_3	CH_3	C_6H_5	$—(CH_2)_3—$
6	2	Cl	Cl	CH_3	CH_3	$CH_3CH=$
7	2	Cl	Cl	CH_3	CH_3	$—(CH_2)_2—$

In this preliminary communication, we describe the synthesis of 1,3-disilacyclohexanes, which were obtained both by the basic reaction (1) and by closure of a second type (2).



(2)

The properties of the products obtained by schemes (1) and (2) (SRS spectra, boiling point, n_D^{20}, d_4^{20} or $R=R^1=R^2=R^3=R^4=CH_3$) were found to be identical.

It particular, it is important to note that the proposed method makes it possible to obtain heterocycles containing functional groups on the silicon atoms. In addition, the given method produces a possible synthesis of compounds containing asymmetric silicon atoms. The starting polyfunctional compounds for cyclization were obtained by addition of silane hydrides containing chloromethyl or γ-chloropropyl radicals to vinyl- and allylchlorosilanes.

Their structure and properties will be reported later in greater detail.

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EXPERIMENTAL

1,1,1-Trichloro-5,5-dimethyl-5-chloromethyl-1,5-disilpentane. The addition reaction was carried out by the method presented in [7]. From 121 g of allyltrichlorosilane, obtained by direct synthesis (bp 114-115°; n_D^{20} 1.4470; 60.5% Cl), and 75 g of chloromethyldimethylsilane (bp 79.5-81.5°; n_D^{20} 1.4167) was obtained 150 g of 1,1,1-trichloro-5,5-dimethyl-5-chloromethyl-1,5-disilpentane having bp 110-112° (4-5 mm); n_D^{20} 1.4750; mol. wt. found* 280; 276; calculated 284; Cl found 37.1; 37.15%; calculated 37.3%.

1-Chloro-1,1,5,5-tetramethyl-5-chloromethyl-1,5-disilpentane. Analogously, from 100 g of allyldimethylchlorosilane (bp 110-114°; n_D^{20} 1.4300; 26.1% Cl) and 81 g of chloromethyldimethylsilane was obtained 137 g of 1-chloro-1,1,5,5-tetramethyl-5-chloromethyl-1,5-disilpentane having bp 113-117° (12 mm); n_D^{20} 1.4611; mol. wt. found 251; 256; calculated 243; Cl found 14.90; 14.80%; calculated 14.60%.

1,1-Dichloro-3,3-dimethyl-1,3-disilacyclohexane. In a 3-liter three-necked flask fitted with a stirrer, dropping funnel, and reflux condenser was placed a mixture of 150 g of 1,1,1-trichloro-5,5-dimethyl-5-chloromethyldisylpentane, 2 liters of abs. ether, and 40 g of finely ground magnesium filings. The mixture was heated on a water bath with intense stirring and refluxing of ether for 40 h. Normal workup yielded 76 g of 1,1-dichloro-3,3-dimethyl-1,3-disylacyclohexane having bp 80-81° (10 mm); n_D^{20} 1.4792; d_4^{20} 1.0933; MR found 55.33; calculated 55.56; Cl found 33.20, 33.40%; calculated 33.33%.

1,1,3,3-Tetramethyl-1,3-disilacyclohexane. Analogous to the preceding experiment, from 125 g of 1-chloro-1,1,5,5-tetramethyl-5-chloromethyl-1,5-disilpentane and 37 g of Mg was obtained 39 g of 1,1,3,3-tetramethyl-1,3-disylacyclohexane having bp 168-170°; n_D^{20} 1.4548; d_4^{20} 0.83098; mol. wt. found 172.2; 171; calculated 172.43; MR found 56.28; calculated 56.3.

From 64 g of chloromethyl-γ-chloropropyldimethylsilane (bp 210-214°; n_D^{20} 1.4660), 16.6 g of Mg, and 45 g of dimethylchlorosilane by the method of [6] was obtained 12.4 g of 1,1,3,3-tetramethyl-1,3-disilacyclohexane.

The constants of the product obtained did not differ from the constants of the compound isolated in the preceding experiment.

1,1-(Trimethylene)-3,3-dimethyl-1,3-disilacyclohexane. Analogously, from 37 g of γ-chloropropylchloromethyldimethylsilane, 10 g of Mg, and 27.6 g of 1,1-dichloro-1-silacyclobutane by the method of [6] was obtained 10 g of 1,1-(trimethylene)-3,3-dimethyl-1,3-disilacyclohexane having bp 70-71° (2-3 mm); n_D^{20} 1.4870; d_4^{20} 0.9043; MR found 58.69; calculated 58.8; mol. wt. found 184; 183; calculated 184.37.

1,3-Dimethyl-1-chloro-3-phenyl-1,3-disilacyclohexane. From 80 g of 1,1-dichloro-1,5-dimethyl-5-phenyl-5-chloromethyl-1,5-disilpentane (bp 161-165° (2 mm); n_D^{20} 1.5252; 21.80% Cl), obtained by the known method [7], and 20 g of Mg under the conditions of synthesis of 1,1-dichloro-3,3-dimethyl-1,3-disilacyclohexane was obtained 20 g of 1,3-dimethyl-1-chloro-3-phenyl-1,3-disilacyclohexane having bp 140-141° (5 mm); n_D^{20} 1.5330; mol. wt. found 253; calculated 254.5; Cl found 14.30; 14.40%; calculated 13.80%.

CONCLUSIONS

1. A general method was developed for synthesis of silicon–carbon heterocycles of the 1,3-disilacycloalkane series, based on an intramolecular cyclization reaction of α,ω-polyfunctional organosilicon compounds containing two types of reaction centers: the Si – X and Si – R – X groups [X is a halogen, R is $(CH_2)_x$].

2. The method makes it possible to prepare silicon-functional disilacycloalkanes, among them those containing asymmetric silicon atoms.

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*Molecular weights were determined cryoscopically in benzene.

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